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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

INVESTIGATION OF AN INTERMETALLIC COMPOUND FORMED IN IRON-TITANIUM ALLOYS

R. B. Golubtsova

(Presented by Academician I. P. Bardin, July 4, 1957)

Investigations devoted to the study of the system iron-titanium have been described in the literature [1].

Lamort [2] established the presence of the intermetallic compound Fe_3Ti, which melts at 1397° without decomposition, in alloys containing 220 wt. % Ti. Other investigators [3, 4] also concluded that this compound exists. Further, the investigations of Witte and Walbaum [5] of alloys containing 18-40% Ti established the presence of the intermetallic compound Fe_2Ti with a crystalline lattice approximating that of $MgZn_2$ and with a melting point of about 1530°.

The work of Duwez and Taylor [6], which was devoted to an x-ray investigation of Fe–Ti alloys, confirmed the presence of the compound Fe_2Ti with a hexagonal lattice with the parameters: $\underline{a}$ = 4.769 A, $\underline{c}$ = 7.745 A, and c/a = 1.624.

In connection with investigations of titanium alloys carried out in the Laboratory of Chemistry of Metallic Alloys, Institute of Metallurgy, Academy of Sciences USSR, by I. I. Kornilov and N. G. Boriskina [7] and co-workers on the study of the titanium–iron structural diagram, it was of interest to investigate the compositions of the compounds formed in this system. The structural diagram of this system is presented in Fig. 1.

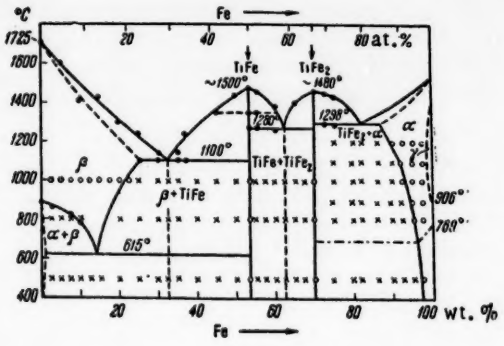

Fig. 1.

In the present paper are presented the results of an investigation concerned with the separation and determination of the composition and structure of the compound Fe_2Ti. For this purpose, we used two cast alloys prepared by N. G. Boriskina and having the following chemical compositions: 1) Fe = 98.99%; Ti = 1.02%; 2) Fe = 83.0%; Ti = 16.73%.

According to the structural diagram (see Fig. 1), the alloy of the first composition corresponds to a solid solution of titanium in iron, and the content of the compound Fe_2Ti in the alloy was approximately 57%.

The samples of annealed, cast alloys were cylindrical in shape with a length of 3.10 cm and a diameter of 0.45 cm. In order to select the optimum electrolyte composition, electrode potentials were measured for the solid solution alloy containing 98.99% Fe and 1.02% Ti and for the alloy containing the Fe_2Ti phase.

The measurements were made with respect to the saturated calomel electrode [8, 9].

The data obtained are presented in Table 1.

TABLE 1
Electrode Potentials, in mv, for Fe_2Ti Phase and Solid Solution

Expt. No.	Electrolyte composition	Fe_2Ti Phase	Solid solution of Ti in Fe	pH of electrolyte
1	2% HCl	−116	−216.7	1.0
2	1% $HClO_4$	−156	−222.0	1.2
3	1% HNO_3	−150	−149.7	1.0

TABLE 2
Effect of Current Density on the Anodic Separation of Fe_2Ti Phase in 2% HCl after 15 Minutes

Expt. No.	Current density, amps/sq. cm.	Decrease in weight of anode, g	Weight of powder collected, g	Found, wt. %			
				Fe	Ti	Total	Fe:Ti
1	0.10	0.3632	0.1910	70.10	29.86	99.96	2.35
2	0.05	0.1233	0.0509	70.16	30.00	100.16	2.33
3	0.02	0.0290	0.0112	69.83	30.10	99.93	2.32

As seen from Table 1, the best electrolytes for the phase separation were Electrolytes Nos. 1 and 2, and the electrode potential was almost the same in Electrolyte No. 3, but there was no liberation of powder. The current density had a substantial effect on the formation of powder.

The experiments carried out on the anodic solution of the Fe−Ti alloy in 2% (by volume) HCl at different current densities (Table 2) showed that the best results with respect to yield of powder separated were obtained at a current density of 0.1 amps./sq. cm. It is important to note, in these experiments, the absence of an effect of current density on the purity of the separated phase (the absence of solid solution impurity).

As a result of anodic solution of the Fe−Ti alloy, over the course of 15 minutes the precipitate formed was deposited on the test anode as a dense layer. At the conclusion of an experiment, the test anode was immersed in distilled water and then in alcohol, after which the powder was scraped with a knife blade into a small cell.

Drying of the cell with the deposit was carried out in a closed quartz test tube in a current of hydrogen (a general view of the powder is shown in Fig. 2). The test tube was heated in an oil bath at 120°. The dried powder was subjected to x-ray and microchemical analysis. A weighed sample of the powder was dissolved in HCl (1:1); after oxidation of the solution with nitric acid and boiling, the iron was precipitated with ammonia, heated, and filtered, and the precipitate subsequently dissolved in hot hydrochloric acid. After transferring the solution to a volumetric flask, volumetric determination of the iron was carried out on an aliquot portion of the solution by complex formation with Trilon B [10] (the disodium salt of ethylenediaminetetraacetic acid) using 20% sulfosalicylic acid as the indicator.

Preliminary experiments with synthetic Fe−Ti mixtures showed that this method of determining iron, which we used in the presence of considerable amounts of titanium, is reliable and accurate. Good reproducibility of the analytical results was obtained. Determination of the titanium was carried out on an aliquot portion of the solution (after evaporation with sulfuric acid) by a colorimetric method using hydrogen peroxide.

The results of the microchemical analyses of the anode powders separated in the various electrolytes are presented in Table 1.

The results, which exhibit good reproducibility (Table 3), show that the iron-titanium alloy investigated contained the metallic compound Fe_2Ti of stoichiometric composition with a ratio Fe:Ti of 2.33:1 (wt. %) and 2:1 (at. %), which is in complete agreement with the theoretical ratio of iron and titanium in the compound Fe_2Ti. The results of the experiments attest to the purity of the liberated phase (absence of a solid solution of iron in the Fe_2Ti).

The results of x-ray structural analysis of the separated anode powders confirm the presence of the compound Fe_2Ti having a hexagonal lattice with the parameters a = 4.769 A, c = 7.745 A, c/a = 1.624 (Figs. 3 and 4).

TABLE 3

Results of Microchemical Analyses of Iron-Titanium Anode Powders (Current density 0.1 amps./sq. cm., experiment time 15 minutes)

Expt. No.	Electrolyte composition	Decrease in wt. of anode	Wt. of powder collected, g	Yield of phase, %	Wt. of powder used for analysis, g	Found, wt. %				Found, wt. %				Conclusions from x-ray structural analysis
						Fe	Ti	Total	Ti : Fe	Fe : Ti	Ti	Total	Ti : Fe	
1	2% HCl	–	[illegible]	–	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–
2	2% HCl	0.3632	0.1910	52.62	0.0291	70.10	29.86	99.96	2.35	66.84	33.15	99.99	2.01	Hexagonal lattice Fe_2Ti a = 4.769 A c = 7.745 A
3	1% HCl	0.1219	0.0608	49.87	0.0352	70.04	29.58	99.62	2.36	67.35	32.70	100.05	2.05	
4	20% HCl	0.0554	0.0173	31.23	0.0128	69.46	30.50	99.96	2.28	65.82	34.14	99.96	1.92	
5	1% $HClO_4$	0.5501	0.2438	44.31	0.0316	70.10	30.00	100.10	2.34	66.84	33.15	99.99	2.01	
6	2% $HClO_4$	0.1003	0.0501	49.95	0.030	69.96	30.00	99.96	2.33	66.65	33.34	99.99	2.0	Hexagonal lattice
7	0.5% $HClO_4$	0.1111	0.0397	35.73	0.0240	69.95	29.91	99.86	2.33					Fe_2Ti a = 4.768 A
8	0.5% H_2SO_4	0.0453	0.0163	35.98	0.0115	70.20	29.76	99.96	2.35	66.92	33.13	100.05	2.02	c = 7.445 A

TABLE 4

Material Balance Around the Electrolysis

	Experiment No. 1	Experiment No. 2	Experiment No. 3	Experiment No. 4
Current density, amps./sq. cm.	0.05	0.02	0.1	0.1
Electrolyte	2% HCl	1% $HClO_4$	2% HCl	0.5% $HClO_4$
Weight of dry anode powder, g	0.0509	0.03420	0.1910	0.03970
Found in electrolyte after separation of phases, g				
Fe	0.0699	0.02390	0.1719	0.07287
Ti	0.0044	0.00028	0.0052	0.00143
Total	0.1252	0.05838	0.3681	0.11400
Decrease in weight of anode	0.1233	0.0578	0.3632	0.1111

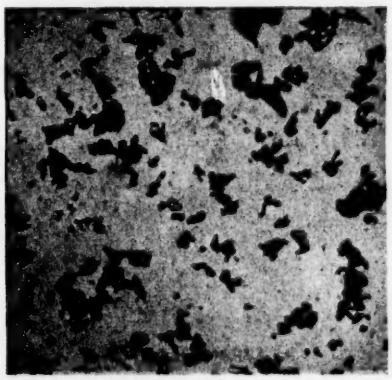

Fig. 2

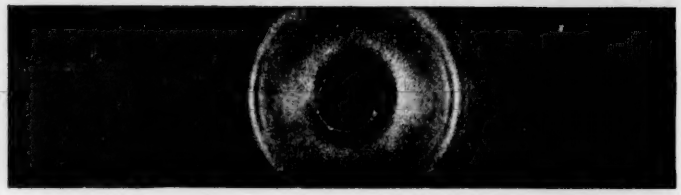

Fig. 3

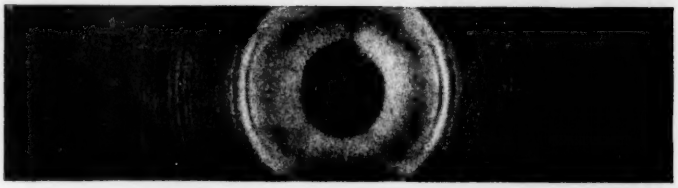

Fig. 4

Material balances of the electrolysis products from the various electrolytes (at different current densities) showed good agreement with the loss in weight of the anodes (Table 4).

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DIMERIZATION OF BUTYRALDEHYDE AT SUPER-HIGH PRESSURES

M. G. Gonikberg and B. S. El'ianov

(Presented by Academician B. A. Kazanskii, July 13, 1957)

In 1929, P. W. Bridgman and J. B. Conant [1] discovered the phenomenon of the polymerization of butyraldehyde at room temperature and a pressure of 12,000 atm. Subsequent work [2, 3] established that this reaction is initiated by small amounts of oxygen and peroxides. The resulting polymer had consistencies ranging from a thick liquid to a wax, and gradually depolymerized at atmospheric pressure with the formation of the original aldehyde. The rate of depolymerization depended to a considerable degree on the temperature. According to the data of reference [3], the polymers can be stored under vacuum over calcium chloride at 5° for a long period of time. The polymers were insoluble in organic solvents; hence it was impossible to determine their molecular weights. The addition to the polymerizing aldehyde of various reagents for establishing the nature of the terminal groups of the polymer molecules did not give positive results.

Thus, up to the present, the structure of the butyraldehyde polymers and the reasons for their extreme instability remain obscure. It seemed to us that the answers to these questions first require an attempt to prepare, under super-high pressure conditions, lower polymers of butyraldehyde which would be practicable for physiochemical investigation. In the present communication are presented the results of work leading to the preparation of an unstable dimer of butyraldehyde.

EXPERIMENTAL

In the experiments, we used butyraldehyde which, after drying with calcium chloride, was distilled in a fractionating column equivalent to 30 theoretical plates (in an atmosphere of oxygen-free nitrogen); b.p. 74.3-74.7° (748 mm, n_D^{20} 1.3793-1.3801). The corresponding literature data are contradictory (b.p. 73-77°, n_D^{20} 1.38433 [4]; b.p. 73-74°, n_D^{20} 1.37875 [5]; b.p. 74.7° [6], etc.). Butyraldehyde which had been purified by preparation of the bisulfite-addition compound and its subsequent decomposition had the same constants given above; however, the yield was extremely low owing to the occurrence of condensation processes during the bisulfite-addition compound with solutions of sodium hydroxide and sodium carbonate.

Experimental method. The freshly distilled butyraldehyde was injected under nitrogen, by means of a syringe, into a brass sylphon bellows having a volume of about 2 ml; the bellows was fitted with a long outlet tube which, after filling of the bellows, was pinched in two places (Fig. 1). The bellows was then submerged in ice water up to the first crimp in the tube, and the opening in the outlet tube was sealed with tin. The sealed bellows was placed in a high-pressure multiplier (see [7]) ; isopentane was used as the pressure transfer medium. The pressure was measured with a manganin gage placed in the channel of the container of the high-pressure multiplier; the accuracy of ±100 atm. The bellows containing the aldehyde was held under pressure at room temperature for the desired time, after which the pressure was lowered and the bellows removed from the multiplier.

Method of determining the polymer yield. About 1.5 g of reaction product was transferred to a cylindrical Duralumin cell (cell weight 2.70 g, height 80 mm, internal diameter 10 mm), which was suspended from a spring balance. The balance, which was a tungsten wire spiral, was placed in a tall glass tube sealed at one end and open at the other end for application of a vacuum. The accuracy of the weight measurements with the spring balance was ± 0.005 g. A vacuum was then applied to the tube (13-18 mm Hg residual pressure). Owing

Fig. 1. Sealed sylphon bellows.

to the rapid vaporization of the unpolymerized butyraldehyde, the cell was cooled to a temperature of about −5° (which inhibited depolymerization of the polymer [3]). During this process, an approximately constant decrease in weight per unit time was established and remained until the monomer was completely vaporized; the slope of the "weight*−time" curve then began rapidly to decrease, and it attained a new constant value. A typical vaporization curve is presented in Fig. 2. The ordinate of the point A on the "weight−time" curve, which corresponds to the beginning of the establishment of the constant vaporization rate after the removal of the original monomer, was taken as the yield of polymer in a given experiment.

In order to evaluate the error in the method, we determined the compositions of synthetic binary mixtures of butyraldehyde (n_D^{20} 1.3798) and butyl butyrate (which corresponds in empirical formula to the dimer of butyraldehyde) with n_D^{20} 1.4063; n_D^{25} 1.4043 (according to the data of [8], n_D^{25} 1.4045). The results of these experiments are presented in Table 1.

Inspection of Table 1 leads to the conclusion that use of the method described above permits approximate determination of the composition of mixtures consisting of components with markedly different saturated vapor pressures and molecular weights. The contents of the higher-molecular-weight component obtained by this method were somewhat too high (by 2.5-5%).

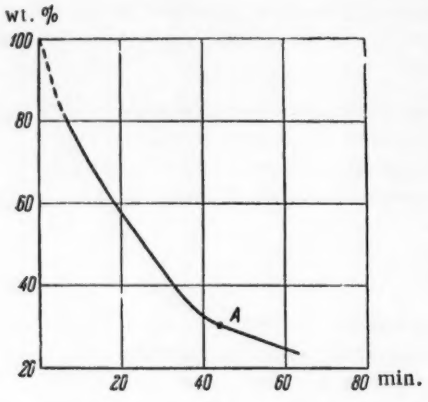

Fig. 2. Polymerizate vaporization curve.

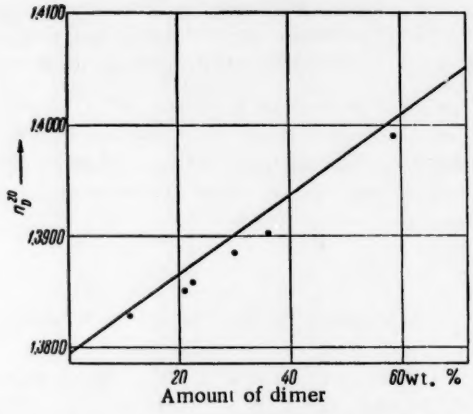

Fig. 3. Dependence of refractive index of polymerizate on dimer content. Points denote dimer content according to vaporization curves.

TABLE 1

Analysis of C_4H_8O + $C_8H_{16}O_2$ Mixtures

Content of $C_8H_{16}O_2$ in the mixture, wt. %		Absolute error, %
Actual	Found	
20	22.5	+ 2.5
40	45	+ 5
60	65	+ 5

Results of the investigation. Our experiments showed that liquid polymer can be obtained from butyraldehyde at pressures of 5500-6000 atm. This requires adherence to the above-described method for the preparation of the aldehyde and for filling the bellows with it, and sealing the latter. Experiments carried out under conditions permitting contact of the aldehyde with air led, in a number of cases, to the preparation of a waxy product. Polymerization was not detected at 3000 atm. The liquid polymers were soluble in benzene, which permitted determination of their molecular weights. The results of some of the experiments are reported in Table 2.

* Expressed in per cents of the weight of polymer taken.

TABLE 2

Results of Experiments on the Dimerization of Butyraldehyde

Expt. No.	P, atm.	Duration of experiment, hours	n_D^{20} of aldehyde	n_D^{20} of polymer**	Mol. wt. of polymer
1	3000	25	1.3795	Polymerization not detected	
2*	5500	24	1.3801	1.4145	142
3*	5500	48	1.3801	1.4221	164
4	6000	23	1.3801	1.4143	137
5	6000	24	1.3793	1.4178	–
6	6000	23	1.3707	–	143
7	6000	21	1.3795	1.4121	–
8	6000	9	1.3800	1.4141	–

* Experiments Nos. 2 and 3 were carried out in parallel in two multipliers using the same initial aldehyde.
** After vaporization of the unpolymerized aldehyde.

Consideration of Table 2 permits the conclusion that, under the conditions studied, polymers having a molecular weight close to that of the dimer (144) were formed from butyraldehyde.

In Fig. 3 is shown the relationship between the refractive index of the polymerizate and the dimer content (Experiments Nos. 2, 4-8*). The straight line on this graph was plotted assuming additivity of n_D^{20} for monomer and dimer (on a weight basis; n_D^{20} of the dimer was taken as 1.4150). As seen from the figure, the experimental points lie to the right of this line, the derivation reaching 5% in the direction of a greater content of dimer.

These polymers gradually depolymerized in air at atmospheric pressure. However, the rate of depolymerization was insignificant in dilute solutions of the polymer in benzene at temperatures close to the freezing point of the latter. Thus, in Experiment No. 2 the molecular weight decreased from 142 to 135 in 47 minutes, and in Experiment No. 6 it decreased from 143 to 134 in 33 minutes, which is substantially within the limits of error of the determinations.

We also carried out experiments to determine whether significant depolymerization of the butyraldehyde polymer occurred at the time of the solution in benzene.

We mixed the dimer from Experiment No. 5 (n_D^{20} 1.4178) with benzene (n_D^{20} 1.5010). This mixture, which contained 32 wt. % dimer, was characterized by n_D^{20} 1.4728; calculated on an additivity basis n_D^{20} 1.4744. Taking into account that some depolymerization occurred during weighing of the polymer and also the possibly approximate nature of the additivity basis, it can be asserted that no significant amount of depolymerization of the polymer occurred during its solution in the benzene and that, consequently, the polymer molecular weights obtained by us were close to the true values.

Thus, an unstable dimer of butyraldehyde was obtained (at pressures of 5500-6000 atm.) for the first time in the present work. The structure of this dimer and the reasons for its instability constitute the subject of a future investigation.

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*The yields of polymer in the various experiments differed considerably from each other, apparently as a consequence of our failure to provide for complete identity of the properties of the monomer and of the experimental conditions.

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ALKYLATION OF BIPHENYL WITH PSEUDOBUTYLENE [2-BUTENE] IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$ CATALYST

S. V. Zavgorodnii and V. I. Sidel'nikova

(Presented by Academician A. V. Topchiev, August 5, 1957)

In an extension of previous investigations in the field of alkylation of aromatic compounds with olefins in the presence of catalysts based on boron trifluoride, we studied the reaction of biphenyl with pseudobutylene [2-butene] in the presence of $BF_3 \cdot H_3PO_4$. The reaction was studied at various mole ratios of biphenyl, pseudobutylene, and catalyst without a solvent and in solution in CCl_4 in the temperature range 5-100°. The investigations established that biphenyl is alkylated by pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$ at mole ratios of 1-4:1:0.2-0.3 and at 50-100° with the formation of monobutylbiphenyl as the basic products. At temperatures of 70° and higher, the process is accompanied by isomerization of the pseudobutylene to isobutylene, which leads to the formation of a mixture of p-sec-butylbiphenyl and p-tert-butylbiphenyl. The relative amounts of these compounds depends on the temperature and other factors. For example, when biphenyl is reacted with pseudobutylene and $BF_3 \cdot H_3PO_4$ in mole ratios of 1:1:0.2, a temperature of 70°, and a feed rate of pseudobutylene of 5.5-6 liters/hour , monobutylbiphenyls are obtained with a yield of 46.4% of theoretical. The relative contents of secondary and tertiary butylbiphenyls comprise, respectively, 81 and 19%. Sec-butylbiphenyl and tert-butylbiphenyl are obtained in approximately the same yield (47.2%) at a temperature of 90°, but their relative amounts in the mixture are changed and are equal to, respectively, 58 and 42%. At a ratio of reagents and catalyst of 2:1:0.2 and a temperature of 90°, monobutylbiphenyls are formed with an overall yield of 38.8% of theoretical, and the relative contents of p-sec-butylbiphenyl and p-tert-butylbiphenyl are, respectively, 74% and 26%.

The most favorable conditions, at which monobutylbiphenyls are formed with a yield of 58-60% of theoretical and with a relative content in the alkylate of up to 92%, are a mole ratio of biphenyl to pseudobutylene to $BF_3 \cdot H_3PO_4$ of 1.75:1:0.25, a temperature of 90°, and a pseudobutylene feed rate of 2.5-3 liters/hour.

A decrease in the amount of catalyst to 0.13 mole under the indicated conditions reduces the yield of monobutylbiphenyls to 32%. An increase in the amount of biphenyl to 3 and 4 moles per mole of pseudobutylene also decreases the yield of monobutylbiphenyls to 19-29%, but polybutylbiphenyls are practically absent from the alkylate under these conditions. When the reagents and catalyst are present in a ratio of 1:1:0.2, monobutylbiphenyls are obtained with a yield 43-45% and polybutylbiphenyls with a yield of 7-8% of theoretical.

The alkylation of biphenyl with pseudobutylene in solution in CCl_4 proceeds very slowly, and at mole ratios of reagents and catalyst of 1:1:0.15, 1:1:0.3, and 3:1:0.3, it gives monobutylbiphenyls with a yield of, respectively, 12, 14, and 18% of theoretical.

EXPERIMENTAL

The biphenyl required for the reaction was the commercial product with m.p. 70°. The pseudobutylene was recovered from a pseudobutylene-butadiene fraction from the manufacture of SR (synthetic rubber) by polymerization of the butadiene with metallic sodium. Prior to use, it was purified from traces of isobutylene by passage through a column containing 68% sulfuric acid, and dried with calcium chloride.

The reaction was carried out similarly to the alkylation of benzene with pseudobutylene [1]. At temperatures up to 70°, solvent was used in an amount of 200 ml of CCl_4 per mole of biphenyl. After the introduction of the specified amount of pseudobutylene, the reaction mixture was stirred at the same temperature for 2 hours and allowed to stand at room temperature for some time. The hydrocarbon layer was then washed with water, a 5% solution of soda, again with water, dried with calcium chloride, and distilled. The solvent, CCl_4, was evaporated at atmospheric pressure, and the residue was distilled under vacuum from a Favorskii flask. In almost all experiments, a small amount of low-molecular-weight polymer of the olefin was distilled first. The alkylation products were distilled into fractions boiling from 7 to 20° above the biphenyl cut point. From 0.1 to 1 g of a dark brown, viscous oil always remained in the distillation flask.

p-Tert-butylbiphenyl usually crystallized from the butylbiphenyl fractions on standing, and was separated from the liquid p-sec-butyl -biphenyl by filtration.

For the separation of the pure products, the butylbiphenyl fractions from several experiments were combined and distilled in a rectification column equivalent to 20-25 theoretical plates. The relative content in the mixture of secondary and tertiary butylbiphenyls was determined by separately distilling the alkylate from specific experiments. During the distillation, the p-tert-butylbiphenyl distilled in a 1° range and immediately crystallized, and then the sec-butyl-biphenyl was distilled at the same temperature or 1-2° higher. We were unable to separate individual products from the polybutylbiphenyls. The most characteristic experiments are summarized in Table 1.

p-Sec-Butylbiphenyl was a colorless, almost odorless liquid. It contained traces of p-tert-butylbiphenyl, b.p. 117.5°/2 mm; d_4^{20} 0.9762; n_D^{20} 1.5718; MR_D 71.52, calc. 68.87.

Found %: M 208.0, 213.2. $C_{16}H_{18}$. Calculated %: M 210.1.

The monobromide of p-sec-butylbiphenyl, obtained by bromination of the hydrocarbon in CCl_4 in the presence of iron filings with a yield of 82%, was in the form of colorless crystals. After recrystallization from alcohol, it had a m.p. of 98-99°.

Found %: Br 27.93, 28.13. $C_{16}H_{17}Br$. Calculated %: Br 27.66.

Autooxidation of p-sec-butylbiphenyl. In a glass column, containing a sealed-in Schott filter, was placed 24.3 g (0.1 mole) of the hydrocarbon, 0.4 mg of manganese resinate, and 14 mg of NaOH, and air was passed at a rate of 0.1-0.2 liter/minute through the mixture for a period of several hours. 3% isopropylbenzene hydroperoxide was then added, and the passage of air was continued. After 32 hours, the concentration of hydroperoxide in the solution, determined iodometrically, had reached 22%.

Cleavage of the hydroperoxide. To 0.1 g of BaO_2 and 3 drops of 79% H_2SO_4, 0° and with continuous stirring, was added dropwise 10 g of 16.2% p-sec-butylbiphenyl hydroperoxide. An additional 3 drops of H_2SO_4 was then introduced, and stirring was continued. During this, the mixture was heated to 50°. On cooling to room temperature, a voluminous precipitate was formed. The reaction mixture was treated with a 10% solution of NaOH, and the alkaline solution was separated and acidified with hydrochloric acid. 1.13 g, 99.3% of the theoretical yield, of p-hydroxybiphenyl was obtained, which, after two recrystallizations from benzene, had a m.p. 163-164°. The literature [2] gives a m.p. of 164-165°. The methyl ether obtained from the p-hydroxybiphenyl had a m.p. of 87-88°. The literature reports a m.p. of 90° [3].

p-Tert-butylbiphenyl was in the form of colorless plates with a m.p. of 50-51.5° (from alcohol). The literature reports a m.p. of 52° [4]. During the distillation of the alkylate from a Favorskii flask into wide-boiling fractions, it distilled over together with the p-sec-butylbiphenyl and crystallized from it on standing. In a rectification column equivalent to 20-25 theoretical plates, it distilled at 112-113°/1 mm and at 146-147°/5 mm, and immediately crystallized. A mixed sample of this product with p-tert-butylbiphenyl obtained by alkylation of biphenyl with isobutyl alcohol [4] showed no depression of the melting point.

Monobromide of p-tert-butylbiphenyl, prepared by bromination of the hydrocarbon in CCl_4 in the presence of iron filings, was in the form of odorless, colorless crystals with a m.p. of 132-133°.

Found %: Br 27.85, 28.03. $C_{17}H_{17}Br$. Calculated %: Br 27.66.

TABLE 1

Alkylation of Biphenyl with Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$

Expt. No.	Used for the reaction, g			Mole ratio of reagents and catalyst	Reaction temperature, °C*	Butylene feed rate, liters/hour	Monobutylbiphenyls obtained				
	Biphenyl	Pseudobutylene	$BF_3 : H_3PO_4$				g	% of theoretical	B. p., °C (mm Hg)	n_D^4	d_4^{20}
1	38.50	16.27	6.21	1 : 1 : 0.15	65	3.5—4	7.59	12.3	119—129/2	1.5700	0.9748
2	154	58.3	33.20	1 : 1 : 0.2	70	5.5—6	101.4	46.4	124—142/3	1.5756	0.9730
3	38.48	14.92	8.31	1 : 1 : 0.2	90	4.5—5	24.79	47.2	136—143/3	1.5740	0.9724
4	38.50	16.97	12.47	1 : 1 : 0.3	55	4.5—5	9.00	14.2	113—128/2	1.5638	0.9618
5	38.56	8.29	4.18	1.75 : 1 : 0.13	90	2.5—3	10.10	32.5	139—146/3	1.5710	0.9741
6	38.50	8.27	6.20	1.75 : 1 : 0.25	50	1	4.62	15.0	108—119/1	1.5690	0.9734
7	38.57	8.19	6.21	1.75 : 1 : 0.25	90	2	17.78	57.9	126—143/3	1.5728	0.9736
8	38.86	8.73	8.33	1.75 : 1 : 0.3	90	2.5—3	19.42	59.3	121—140/3	1.5729	0.9738
9	154	30.00	16.60	2 : 1 : 0.2	90	5.5—6	43.56	38.8	152—162/8	1.5730	0.9709
10	38.50	6.45	6.20	2 : 1 : 0.3	100	1	9.10	37.6	135—148/3	1.5720	0.9646
11	38.56	7.07	8.31	2 : 1 : 0.4	90	2.5—3	10.09	38.4	160—182/9	1.5728	0.9758
12	58.00	7.38	6.21	3 : 1 : 0.3	60	2.5—3	5.07	18.3	141—154/7	1.5672	0.9682
13	58.07	7.27	6.23	3 : 1 : 0.3	90	2	6.4	23.5	158—160/8	1.5750	0.9768
14	38.50	5.37	6.28	3 : 1 : 0.4	80	0.5—1	9.00	44.7	112—125/2	1.5672	0.9736
15	76.80	7.26	6.22	4 : 1 : 0.3	90	0.5—1	7.91	29.1	160—186/9	1.5713	0.9720

* Temperature variation ± 2.

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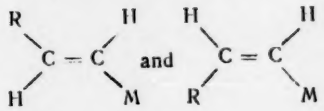
A STUDY OF THE STEREOCHEMISTRY OF SUBSTITUTION REACTIONS AT AN OLEFINIC CARBON ATOM BY THE ISOTOPE METHOD

Academician A. N. Nesmeianov, O. A. Reutov and P. Knoll'

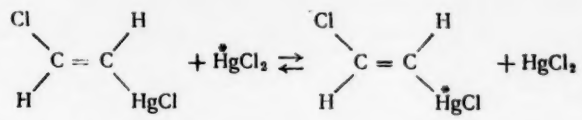
One of us and A. E. Borisov [1], studying the exchange of metal in a series of stereoisomeric organometallic compounds of the type



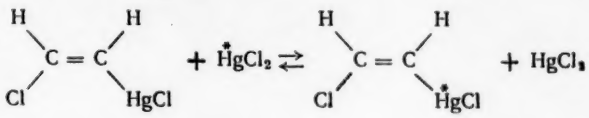
established the following rule: electrophilic and homolytic exchange reactions at an olefinic carbon atom proceed with retention of the cis- and trans-configurations.

In the present work, using the isotope method, we obtained direct proof of the correctness of this rule.

As examples of electrophilic reactions, we studied the interaction of cis- and trans-β-chlorovinylmercury chlorides with mercuric chloride tagged with radioactive mercury, Hg^{203}. The reactions were carried out in acetone solution in the cold. In both cases, we showed that isotope equilibrium is rapidly established (less than 5 minutes) and that the original stereochemical configuration of the chlorovinyl group is strictly maintained during the process:



(1)

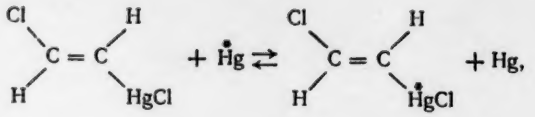


(2)

As examples of homolytic reactions, we studied the interaction of metallic mercury tagged with Hg^{203} with cis- and trans-β-chlorovinylmercury chlorides and also with bis-(cis- and bis-(trans-β-chlorovinyl)mercury.*

All four organomercury compounds readily react in acetone in the cold with finely dispersed metallic mercury. Isotope equilibrium is established after several hours. All of these reactions proceed with complete retention of the stereochemical configuration of the chlorovinyl group:

* The occurrence of an isotope exchange reaction between metallic mercury and symmetrical organomercury compounds and organomercury salts of the aromatic and aliphatic series was established by us previously [2].



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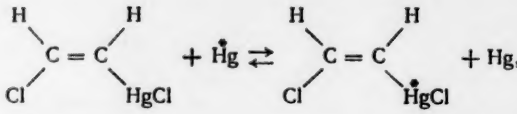

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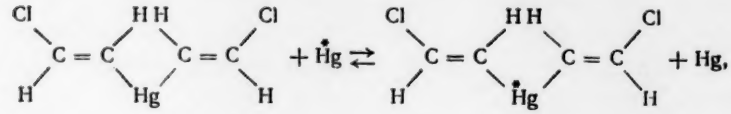
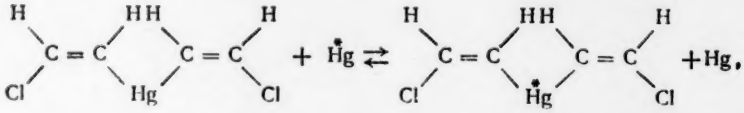


(5)



(6)

During the reaction of metallic mercury with cis- and trans-β-chlorovinylmercury chlorides, in addition to the isotope exchange reaction, a side reaction also takes place with the formation of calomel and acetylene:

$$Cl-CH=CH-HgCl + Hg \rightarrow H-C\equiv C-H + Hg_2Cl_2^{\bullet}. \quad (7)$$

Thus, we have here a typical example of the dual reactivity which is so characteristic of all β-chlorovinyl organometallic compounds.

If the results of isotope exchange of bis(cis- and bis-(trans-β-chlorovinyl)mercury with metallic mercury (Reactions (5) and (6)) are direct proof of the retention of stereochemical configuration during these reactions, the results obtained in Reactions (1)-(4) require further consideration.

During a study of the kinetics of the symmetrization of esters of α-bromomercuriphenylacetic acid by ammonia, I. P. Beletskaia, R. E. Mardaleishvili and one of us [3] showed that the reaction proceeds in two stages.••

(a) $$2R-HgX \rightleftarrows R_2Hg + HgX_2 \quad (a)$$

(b) $$HgX_2 + 2NH_3 \rightleftarrows HgX_2 \cdot (NH_3) \quad (b)$$

If in our Reactions (1)-(4) an equilibrium of a similar type

$$2ClCH=CH-HgCl \rightleftarrows (ClCH=CH)_2Hg + HgCl_2 \quad (8)$$

plays any substantial role, then bis(β-chlorovinyl)mercury and mercuric chloride should enter into isotope exchange reactions with $\overset{\bullet}{Hg}$ and $\overset{\bullet}{HgCl_2}$, respectively. The stereochemistry observed by us for Reactions (1)-(4) should be the result not of one, but of several processes. We established by special experiments, however, that

• Special experiments showed that, under our conditions, calomel tagged with Hg^{203} does not enter into an isotope exchange reaction with β-chlorovinylmercury chlorides.

•• Studying the symmetrization of organomercury salts under the influence of KI, Whitmore [4] came to the conclusion that this reaction proceeds through an equilibrium stage.

bis-β-chlorovinylmercury is not present in the reaction mixture even in the case of Reactions (3) and (4), i.e., when the excess metallic mercury, which readily converts mercuric chloride to calomel, would promote a shift of Equilibrium (8) to the right with the formation of appreciable amounts of the symmetrical organomercury compound.

Thus, it can be asserted that Reactions (1)-(4) do not proceed through an equilibrium, but the $HgCl_2$* and Hg react directly with the β-chlorovinylmercury chlorides. In connection with this, our results are direct confirmation of the retention of configuration at an olefinic carbon atom during electrophylic and homolytic substitution reactions.

EXPERIMENTAL

1. Interaction of trans-β-chlorovinlymercury chloride with mercuric chloride labeled with Hg^{203}. 0.1488 g (0.0005 mole) of trans-β-chlorovinylmercury chloride, m.p. 122°, and 0.1359 g (0.0005 mole) of mercuric chloride tagged with Hg^{203} were dissolved in acetone at 23° in a 25-ml volumetric flask. The solution was transferred to an evaporating dish for concentration and evaporation to dryness in the cold under a stream of air. In order to separate the chlorovinlymercury chloride from the mercuric chloride, the residue was dissolved in 50 ml of ether, and the mercuric chloride was extracted from the ether with five portions (of 50 ml each) of a saturated aqueous solution of sodium chloride. The ethereal solution of chlorovinylmercury chloride was evaporated in the cold, and the residue dried in a desiccator over a mixture of calcium chloride and sodium hydroxide.* After recrystallization from acetone, the trans-β-chlorovinylmercury chloride had a m.p. of 120°. A mixture with a known sample of trans-β-chlorovinylmercury chloride melted at 121°. Prior to the radioactivity determination the trans-β-chlorovinylmercury chloride was twice recrystallized from acetone. The isotope exchange amounted to 99.**

2. Interaction of cis-β-chlorovinylmercury chloride with mercuric chloride labeled with Hg^{203}. 0.1484 g (0.0005 mole) of cis-β-chlorovinylmercury chloride, m.p. 78°, and 0.1355 g (0.0005 mole) of mercuric chloride labeled with Hg^{203} were dissolved in acetone at 23° in a 25-ml volumetric flask. The solution was transferred to an evaporating dish for concentration and evaporation to dryness in the cold under a stream of air. The solid residue was extracted (twice with 20 ml) with carbon tetrachloride. The solution of cis-β-chlorovinylmercury chloride was filtered and evaporated to dryness. The cis-β-chlorovinylmercury chloride was recrystallized from acetone. M.p. 79°. A mixture with a sample of known cis-β-chlorovinylmercury chloride melted at 78° (with a known sample of trans-β-chlorovinylmercury chloride, the m.p. was 92.*** Isotope exchange amounted to 92%.

3. Interaction of trans-β-chlorovinylmercury chloride with metallic mercury labeled with Hg^{203}. A solution of trans-β-chlorovinylmercury chloride in acetone (concentration 0.05 mole/liter) and the metallic mercury (40-fold gram-equivalent excess) were stirred in a 200-ml flask fitted with a reflux condenser, a pipet for sample collection, and a Witt stirrer (3000 ± 200 rpm). The formation of calomel and acetylene was noted for several minutes after the beginning of stirring. Samples for the determination of radioactivity were collected at specific intervals of time, the amounts being so calculated that the total amount of solution collected as samples did not exceed 10% of the amount taken for the reaction.

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* Separation of the mixture of chlorovinylmercury chloride and mercuric chloride can also be accomplished by means of carbon tetrachloride, in which the organomercury compound dissolves and the mercuric chloride is practically insoluble.

** Measurements of the radioactivity of the preparations containing Hg^{203} were carried out in a B-2 apparatus by means of MST-17 end-window counters. The preparations were deposited (by pouring the solutions dropwise) on 20-mm-diameter filters, covered with an organic glass lacquer (5 g of plexiglass in 200 ml of dichloroethane), and dried. The preparations were wrapped in tracing paper, and placed in the center between the windows of two MST-17 counters, which were fixed at the base in a lead IFKh-2 housing and connected in parallel to the cathode of a BGS repeater. In all cases, the experimental error was 5-10%.

*** The curve of the dependence of the melting points of mixtures of cis- and trans-β-chlorovinylmercury chlorides on mixture composition has no minimum (linear relationship).

a) Reaction carried out at 23°:

Exchange time, hours	0.58	1.33	2.33	4.42	6.17
Per cent exchange	7	24	31	53	64

The m.p. of the original material was 122°. The m.p. of the trans-β-chlorovinylmercury chloride isolated from the reaction mixture was 119°. A mixture with a known sample of trans-β-chlorovinylmercury chloride melted at 120°.

b) Reaction carried out at 35°:

Exchange time, hours	1.00	1.33	1.66	2.00	2.50	3.75
Per cent exchange	39	60	65	82	98	97

The melting point of the original material was 122°. The m.p. after the reaction was 119°. A mixture with a known sample of trans-β-chlorovinylmercury chloride melted at 120°.

4. Interaction of cis-β-chlorovinylmercury chloride with metallic mercury labeled with Hg^{203}. The following results were obtained when the reaction of cis-β-chlrorvinylmercury chloride with metallic mercury labeled with Hg^{203} was carried out under the conditions of the preceding experiment.

a) Reaction carried out at 23°:

Exchange time, hours	0.42	1.08	2.00	3.50	4.50
Per cent exchange	8	18	26	36	74

The original cis-β-chlorovinylmercury chloride melted at 79°, after the reaction it melted at 77°. A mixture with a known sample of cis-β-chlorovinlymercury chloride melted at 78°.

b) Reaction carried out at 35°:

Exchange time, hours	0.25	0.58	0.92	1.16	1.42
Per cent exchange	24	36	54	55	65

The original material melted at 79°; after the reaction it melted at 76°. A mixture with a known sample of cis-β-chlorovinylmercury chloride melted at 77°.

5. Interaction of bis-(trans-β-chlorovinyl)mercury with metallic mercury labeled with Hg^{203}. The reaction of bis(trans-β-chlorovinyl)-mercury (0.05 M acetone solution) with metallic mercury (40-fold gram-equivalent excess) labeled with Hg^{203} was carried out under the conditions of Experiments 3 and 4.

a) Reaction carried out at 23°:

Exchange time, hours	2.25	6.58	7.83	10.50
Per cent exchange	20	48	61	71

The m.p. of the original material was 62°. Its m.p. after the reaction was 61°.

b) Reaction carried out at 35°:

Exchange time, hours	1.25	2.25	3.66	5.25	6.25	9.25
Per cent exchange	55	65	85	96	90	100

The m.p. of the original material was 64°. The m.p. after the reaction was 63°.

6. Interaction of bis(cis-β-chlorovinyl)mercury with metallic mercury labeled with Hg^{203}. The reaction of bis(cis-β-chlorovinyl)mercury (liquid) with metallic mercury labeled with Hg^{203} was carried out at 23° under the conditions of the preceding experiment. After 8 hours, the exchange was 90%. Both before and after the reaction, the bis(cis-β-chlorovinyl)mercury reacted with mercuric chloride to give pure cis-β-chlorovinylmercury chloride.

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POLAROGRAPHIC INVESTIGATION OF TRIVALENT ANTIMONY COMPLEXES IN SODIUM FLUORIDE SOLUTIONS

D. Pavlov and D. Lazarov

(Presented by Academician A. N. Frumkin, July 22, 1957)

In 1948, West, Dean and Breda [1] reported data on the polarographic behavior of 30 ions in fluoride solutions. They gave the following brief characterization of antimony: "it has a half-wave potential of $\pi_{1/2} = -0.683$ and for pH = 3 −4.4. The limiting current constant is 5.91. The reduction of Sb^{+++} to Sb^0 is presumed. The wave is well expressed, although there is a pre-wave, which provides a basis for assuming the existence of an equilibrium form of the antimony complex." Taking into consideration this communication and also the fact that the fluoride ion has a small radius and forms stable complexes with many ions, we set ourselves the goal of investigating the behavior of Sb^{+++} in solutions of NaF and of establishing the nature of the resulting complexes.

All of the polarographic investigations were carried out with a "Heyrovsky V-301" polarograph at a temperature of 25.00 ± 0.02°. The pH was determined by means of an LP-5 potentiometer with a quinhydrone or glass electrode. Constancy of the ionic strength was provided by means of 0.5 M KCl. HCl/KCl and CH_3COOH/NH_4OH buffer solutions were used.

Investigations were carried out in parallel by two methods: 1) The dependence of $\pi_{1/2}$ on pH of the solution was studied at constant total concentration of F^-; 2) the variation in $\pi_{1/2}$ with changes in the concentration of F^- was studied at constant pH. The concentration of Sb^{+++} was maintained constant in both cases. Both series of experiments showed that over the entire pH interval of from 1 to 14, Sb^{+++} is bound in various forms in complexes. At a pH of from 1 to 3, Sb^{+++} is free; at a pH of from 3 to 6, a fluoride complex of antimony is formed, which decomposes in the pH interval of 6 to 8; above a pH of 8, complexes are obtained which do not contain F^-; at a pH > 13, an anodic and a cathodic curve are found on the polarogram. These investigations provide a basis for dividing the entire pH region into three parts.

Complexes of Sb^{+++} in Acid Solutions of NaF

The results of several series of experiments are graphically presented as plots of $\pi_{1/2}$ against pH in Fig. 1. In other series of experiments, it was established that the diffusion current strictly obeys the Ilkovich equation in this pH region (from 3 to 6).

In order to determine the composition and instability constant of the resulting complex, it was necessary to ascertain the activity of the fluoride ion. The following equilibria are established in acid solutions: $F^- + H^+ = HF$ ($K_1 = 6.89 \cdot 10^{-4}$) and $HF + F^- = HF_2^-$ ($K_2 = 0.32$). Considering that a part of the F^- is bound to the Sb^{+++} in the complex (we assume that the complex contains $6F^-$), it is possible to write for the overall concentration of fluoride ion, F_{ov}^-, the equation

$$F_{ov}^- = a_{F^-} + \frac{a_{F^-} \cdot a_{H^+}}{K_1} + 2\frac{a_{H^+} \cdot a_{F^-}^2}{K_1 \cdot K_2} + 6Sb^{+++}.$$

This equation was used to calculate the value of a_{F^-} when a fluoride complex of antimony was present in the solution.

Figure 2 shows the dependence of $\pi 1/2$ on log a_{F^-}. The straight line is well described by the equation $\pi 1/2 = -0.950 - 0.120 \log a_{F^-}$. From the slope in this equation, we determined that the composition of the complex corresponded to $[SbF_6]^{---}$, and from the intercept, the instability constant was determined to be $K_C = 10^{36}$. The experiment showed that this complex is stable until the ratio $a_{OH^-}/a_{F^-} = 10^{-8}$, after which it begins to hydrolyze. The solid points in Figs. 1 and 2 correspond to experiments in which this ratio was higher. Consequently, a complex of the type $[SbF_6]^{---}$ was stable to the maximum on the $\pi 1/2$ – pH curves (Fig. 1).

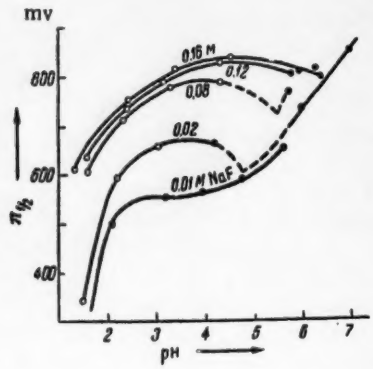

Fig. 1. Variation in $\pi 1/2$ with pH at constant over-all NaF concentration (the value of $\pi 1/2$ was measured relative to a saturated calomel electrode). The ionic strength for all tests was $\mu = 0.3$. Circles correspond to tests for which log a_{F^-} + pH < 6, and the solid points correspond to log a_{F^-} + pH > 6.

Complexes of Sb^{+++} in the Mid-Alkaline Region

This region begins with the decomposition of $[SbF_6]^{---}$, and ends in an alkaline medium (ph of 11-12). In this region, several unstable complexes were obtained. An investigation of the pH interval of from 5 to 8 did not give any single-valued results for $\pi 1/2$, but a minimum was observed in these curves in all cases (Fig. 1). In the pH region of from 8 to 11, two waves were distinguished on the polarogram: the basic wave II and the prewave I (Fig. 3).

The prewave disappeared on standing or heating of the solution, and a white precipitate was obtained. Moreover, it did not depend on the concentration of F^-, and with changes in pH it shifted to more negative values according to the equation $\pi 1/2 = -1.100 - 0.060 \log a_{OH^-}$ (Fig. 4, I). The slope of this equation shows that three OH^- groups take part in this complex. Since an antimony complex must contain more than 4 ligands, we must assume that the remaining coordination sites are occupied by other molecules or ions. These experiments showed that F^-, Cl^-, and NH_3 do not take part in the structure of the complex. Consequently, it must be assumed that the complex $[Sb(OH_2)_{p-3}(OH)_3]$ was formed, which, on standing, split out water and precipitated in the form of $Sb(OH)_3$. The instability constant of this complex is $K_C = 2.7 \cdot 10^{-44}$.

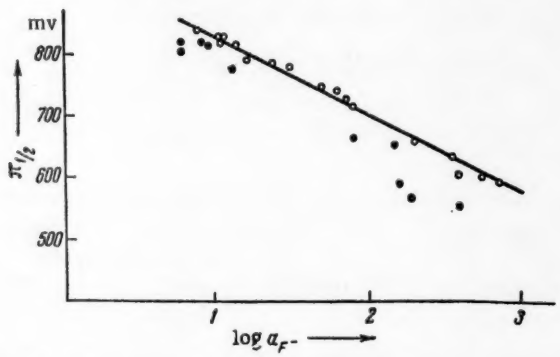

Fig. 2. Dependence of $\pi 1/2$ of the Sb^{+++} wave on log a_{F^-}. $\pi 1/2$. In the pH interval of from 3 to 6, $\pi 1/2$ did not depend on pH of the solution. Solid points correspond to tests in which log a_{F^-} + pH > 6; circles correspond to log a_{F^-} + pH < 6.

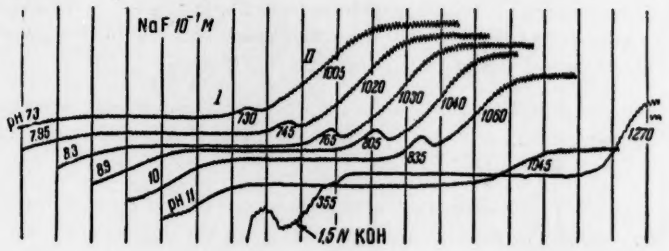

Fig. 3. Polarograms of hydroxy-complexes of Sb^{+++} in freshly prepared solutions. $\pi 1/2$ depends on pH; $1 \cdot 10^{-3}$ M $SbCl_3$; CH_3COOH/NH_4OH buffer solutions. I) prewave, II) basic wave. The lowest curve was taken in a 1.5 N KOH solution, and has an anode and cathode wave ($\pi 1/2$ measured relative to a s. c. e.).

The basic wave also decreased in height, but much more slowly, and the pH of the solutions changed. $\pi^1/_2$ did not depend on the concentration of F^-, Cl^-, or NH_3, and with a change in pH, it shifted to more negative values according to the equation $\pi^1/_2 = -1.150 - 0.020 \log a_{OH^-}$ (Fig. 4, II). This question provides a basis for proposing the following composition for the complex:

$$[Sb(OH_2)_{p-1}(OH)]^{++}, \quad K_c = 10^{-46}$$

The nature of the polarographic wave changed after the solutions had stood for a while. It rose more steeply, and the dependence of $\pi 1/2$ on pH was linear according to the equation $\pi 1/2 = -1.180 - 0.040 \log a_{OH^-}$ (Fig. 4, III). In this case, the complex had the composition $[Sb(OH_2)_{p-2}(OH)_2]^+$, $K_c = 10^{-47}$. These same results could be obtained by heating of the solutions. On standing of the solutions, the precipitate continuously increased, and the height of the wave increased. This proceeded more rapidly in alkaline solutions (at a pH above 12).

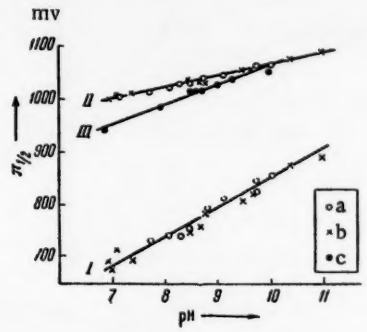

Fig. 4. Variation in $\pi 1/2$ of hydroxy-complexes of Sb^{+++} with pH of the solution. a) solutions containing 0.02 N NaF, b) solutions containing 0.2 N NaF, c) the same solutions after 48 hours. For I, $\pi 1/2 = -1.100 - 0.060 \log a_{OH^-}$, for II, $\pi 1/2 = -1.150 - 0.020 \log a_{OH^-}$, for III, $\pi 1/2 = -1.180 - 0.040 \log a_{OH^-}$.

Investigation of the Behavior of Sb^{+++} in Highly Alkaline Media

This region began with the solution of the precipitate of $Sb(OH)_3$, which was connected with the formation of an alkali salt of metaantimonous acid. A cathodic wave with $\pi_{1/2} = -1.270$ and an anodic wave with $\pi_{1/2} = -0.355$, which was deformed by a peculiar maximum, were obtained in strongly alkaline solutions, at a pH of 14. The heights of the two waves were in the ratio 3:2 (Fig. 3).

The cathodic wave was similar to the wave in 1 N NaOH described by Kacirkova [2] and by Kol'thoff and Lingane [3]. Since the concentration of F^- has no effect on it, it is obvious that the electrode mechanism is the same, $SbO_2^- + 2H_2O + 3e = Sb^0 + 4OH^-$.

The anodic wave was similar in form and value of $\pi_{1/2}$ to that noted by Cozzi [4] in alkaline tartrate solutions ($\pi_{1/2} = -0.360$). Since the same results were obtained in the absence of F^-, we assume the anode reaction:

$$SbO_2^- + 2OH^- = SbO_3^- + H_2O + 2e.$$

Mechanism of the Conversion of the Individual Sb^{+++} Complexes with a Change in Solution pH

In a strongly acid medium (pH of 2-3), the F^- ions are tied up in the form of HF and HF_2^-, and the Sb^{+++} are free. With an increase in pH, the activity of the F^- increases and creates conditions for the formation of $[SbF_6]^{---}$. It is stable until the ratio a_{OH^-}/a_{F^-} is no longer equal to 10^{-8}, after which hydrolysis begins. First of all, the F^- ions are replaced by water molecules, which leads to the formation of $Sb(OH)_p$. The latter takes part in the equilibrium

$$[Sb(OH_2)_p]^{+++} \rightleftarrows [Sb(OH_2)_{p-1}(OH)]^{++} + H^+,$$

which is shifted to the right in an alkaline medium (pH of 8 to 11). The resulting complex is unstable, and on standing decomposes according to

$$[Sb(OH_2)_{p-1}(OH)]^{++} \rightarrow [Sb(OH_2)_{p-2}(OH_2)]^{+} \rightarrow [Sb(OH_2)_{p-3}(OH)_3] \rightarrow Sb(OH)_3 \downarrow .$$

Therefore, in freshly prepared solutions, there is a larger amount of $[Sb(OH_2)_{p-1}(OH)]^{++}$ and an insignificant amount of $[Sb(OH_2)_{p-3}(OH)_3]$. The presence of small amounts of $[Sb(OH_2)_{p-2}(OH)_2]^+$ is possible, but the latter does not give an independent wave, since its value of $\pi_{1/2}$ is very close to that for $[Sb(OH_2)_{p-1}(OH)]^{++}$. On standing, dissociation proceeds with the splitting out of water, the transition from the second to the third stage proceeds most slowly of all, and measurable amounts of $[Sb(OH_2)_{p-2}(OH)_2]^+$ predominate in the solution giving an independent wave.

Detectable hydro- and hydroxy-complexes are unstable, and can be considered only as intermediate forms in the hydrolysis of $[SbF_6]^{---}$. Thus, the presence of F^- ions is necessary, although they do not participate in the formation of the hydroxy-complex.

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STUDY OF ISOTOPE EXCHANGE OF OXYGEN BETWEEN HEAVY-OXYGEN WATER AND CERTAIN NIOBATES AND TANTALATES

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In previous investigations [1-4] on the dehydration of various niobates, we studied the nature of the bound water in these compounds. This work had as its aim clarification of the role of water in the structure of these salts, since different structures are ascribed to these compounds. Süe proposed the general formula $Me_xH_y[(NbO_3)_{12}(OH)_6]\cdot nH_2O$ for niobates [5]. Several other structures were proposed in a paper by Windmaisser [6]: $Me_{16}[(NbO_3)_{12}(OH)_4]\cdot nH_2O$ and $H_{20}[(Nb_3O_{10})_4]$. In the opinion of Jander [7], the structure of the tantalates is described by the formula $Me_7[Ta(TaO_4)_4]$, but the role of water was not taken into account. Halla, Neth and Windmaisser, proceeding on the assumption of the similarity of the structures of niobates and tantalates, proposed the structural formula $Me_{16}[(Ta_{12}O_{36})(OH)_4]\cdot nH_2O$ [8]. On the basis of x-ray investigations, Lindquist [9, 10] found that the structural units of hexaniobates and hexatantalates are the ions $(Ta_6O_{19})^{8-}$ and $(Nb_6O_{19})^{-8}$. He did not determine the position of the water and cations in the compound which he studied. Except for the compounds mentioned in the papers of Lindquist, all of the cited structures, describing, as they do, the behavior of the salts on heating, do not relate to the nature of the bond between the central atom and the oxygen atoms. In the opinion of Nowacki [11], the bond with oxygen is chiefly heteropolar in niobates and tantalates.

Two of us together with Vasil'ev [12] used the isotope exchange method for studying the structure of one of the most important aquopolycompounds of tungsten – sodium paratungstate – and also the normal sodium tungstate. We decided to use this method for studying the structures of certain niobates and tantalates.

The initial niobates and tantalates were prepared by a method described previously [1-3, 13]. Analyses carried out by the usual methods gave the following compositions for the salts:

Sodium pentatantalate – $6.88\ Na_2O\cdot 5Ta_2O_5\cdot 29.1H_2O$;
Sodium hexatantalate – $3.92\ Na_2O\cdot 3Ta_2O_5\cdot 26.1H_2O$;
Potassium hexaniobate – $7.04\ K_2O\cdot 6Nb_2O_5\cdot 22.0H_2O$;
Potassium metaniobate – $0.96\ K_2O\cdot Nb_2O_5\cdot 4.36H_2O$.

The isotope exchange experiments were carried out using water enriched with O^{18} (containing 1.28 at. % O^{18}). The exchange was studied at 95° with saturated solutions of the salts enumerated above. The time of of the exchange was 5 hours in all experiments. Owing to hydrolysis, the solutions of the salts had an alkaline reaction (pH 11-12). The experimental method used in the experiments was described in one of the works cited above [12].

In Table 1 are presented the results of isotope exchange of oxygen between water and the tantalates along with calculated values for the O^{18} content of the solution after complete exchange. As may be seen from the Table, not only oxygen bound as water in these tantalates, but also the oxygen in the anions enters into isotope exchange. Moreover, all of the experimental values of O^{18} content of the water after exchange with the tantalates are characterized by the fact that they are appreciably lower than the calculated values. These deviations exceed the experimental error, since the error in the determination of O^{18} was ± 1% of the measured value. These results can be explained by fractionation of the isotope preferentially in the direction of enrichment of the salts with the heavy oxygen isotope. A similar phenomenon has been noted for sodium paratungstate [12] and certain trivalent ions [14].

TABLE 1

Isotope Exchange of Oxygen Between Heavy-Oxygen Water and Sodium Tantalates. (Content of O^{18} in the original water, 1.28 at. %) (temperature 95°).

Expt. No.	Amounts taken (g)		Content of O^{18} in water after experiment (at. %)		b/a
	salt	water	calculated for complete exchange of O^{18} with all oxygen in the salt (b)	found (a)	
Preparation No. 1 – salt 3.92 $Na_2O \cdot 3Ta_2O_5 \cdot 26.1H_2O$					
1	0.0630	2.0150	1.27	1.22	1.04
2	0.0609	2.0410	1.27	1.22	1.04
3	0.0647	2.0219	1.27	1.24	1.02
Preparation No. 2 – salt 6.88 $Na_2O \cdot 5Ta_2O_5 \cdot 29.1 H_2O$					
1	0.0390	2.0184	1.27	1.22	1.04
2	0.0375	2.0373	1.27	1.23	1.03
3	0.0363	1.9866	1.27	1.23	1.03

TABLE 2

Isotope Exchange of Oxygen Between Heavy-Oxygen Water and Potassium Niobates. (Content of O^{18} in the original water, 1.28 at. %) (temperature 95°).

Expt. No.	Amounts taken (g)		Content of O^{18} in the water after the experiment (at. %)			c/a	b/a
	salt	water	calculated for complete exchange of O^{18}		found (a)		
			with the water of the salt (c)	with all oxygen in the salt (b)			
Preparation No. 1 – salt 7.04$K_2O \cdot 6Nb_2O_5 \cdot 22.0 H_2O$							
1	0.2196	2.0070	1.26	1.23	1.24	1.02	0.99
2	0.2237	2.0165	1.26	1.23	1.22	1.03	1.01
3	0.2296	2.0141	1.26	1.23	1.23	1.02	1.00
Preparation No. 2 – salt 0.96$K_2O \cdot Nb_2O_5 \cdot 4.36 H_2O$							
1	0.2385	1.9910	1.26	1.23	1.24	1.02	0.99
2	0.2223	2.0032	1.26	1.23	1.23	1.02	1.00
3	0.2190	1.9439	1.26	1.23	1.23	1.02	1.00

As seen from the data of Table 2, complete exchange of oxygen of the water–solvent with the bound water and anions of the salts also occurred in the case of potassium hexaniobate and metaniobate. However, enrichment of the salt with the heavy oxygen isotope was not detected in this case. Apparently, the lower molecular weights of the niobates as compared to the tantalates leads to this difference. As regards the tantalates studied, they approximate the aquopolytungstates in this respect.

This investigation shows that in the compounds studied – sodium pentatantalate and hexatantalate and potassium hexaniobate and metaniobate – all of the oxygen atoms in the salt and bound water are available for isotope exchange with the water–solvent. Isotope exchange of oxygen between water and the compounds studied proceeds comparatively rapidly, and equilibrium is attained in the course of 5 hours.

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THE CHEMICAL COMPOSITION OF MAKHACHKALIN PETROLEUM

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The Makhachkalin petroleum deposits are found in the Pricaspian plain two kilometers south of the city of Makhachkala. The petroleum is found in sand beds of the Chokrasko-spirialisov deposits of formation G.

The samples were collected September 26, 1954 from well No. 92.

Physiochemical Characteristics of the Petroleum

The petroleum investigated by us had the following elemental composition (in wt. %):

C	H	S	N+O
83.36	13.48	0.21	0.08
86.23	13.67		0.08

The C and H contents were determined by the method developed in the Central Institute of Aviation Fuels and Oils, which permits automatic opening of the ampoules containing the weighed sample inside the combustion tube. The N content was determined by the modified Kjeldahl method, and the S content was determined by combustion in a bomb calorimeter.

The paraffin content was determined by the acetone-benzene method after freeing the petroleum sample from resins by the method of Marcusson. The yield of gasoline and kerosene fractions was obtained by Gadaskin fractionation, d_4^{20} 0.8340.

Pour point, °C	−23.5	M. p. of paraffin, °C	51.0
Content, %		Coke (Conradson), %	1.57
asphaltenes	0.92	Acid number	0.0672
aktsiznye resins	12.0	Content of fractions, %	
silica gel resins	6.8	to 200°	27.2
paraffin	5.8	to 300°	40.0

Viscosities of the petroleum were as follows:

Viscosity	at 10°	at 20°	at 30°	at 40°	at 50°
Kinematic, sec.	15.27	8.87	5.47	3.82	1.47
Conventional, °E (converted)	2.40	1.66	1.44	1.37	1.05

Engler distillation gave the following fractions:

I. b.p. 45°	120°	140°	150°	180°	200°	220°	240°	260°	280°	300°
Volume, ml	12	18	21	26	30	34	38	42	46	52

Makhachkalin petroleum from well No. 92 belongs to the type of petroleum which has a high gasoline-fraction content (27.2%). The low density, comparatively low resins content (12% aktsiznye resins), and low Conradson carbon (1.57%) with a rather high paraffin content (5.8%) provide a basis for relating this petroleum to the very light type of mixed base petroleum. In conformity with GOST, it is a low-sulfur, low-resin, paraffinic petroleum.

Inover-all properties, the petroleum approximates other Daghestan petroleums.

In order to obtain the fractions required for further study, about 9 liters of the petroleum was distilled in a Gadaskin apparatus. The fractions boiling up to 200° were collected at atmospheric pressure, while those above 200° were collected at pressures of 1-5 mm Hg. During collection of the light fractions (up to 95°), the apparatus was cooled with a mixture of ice and table salt. The gas was not collected.

Gasoline Fractions of the Petroleum

The group chemical composition of the fractions was determined by the aniline point method. Removal of the aromatic hydrocarbons was accomplished by the sulfuric acid and adsorption methods. In the first case, the fractions were treated with $3\frac{1}{2}$ volumes of 98-99% sulfuric acid for 30 minutes. In the second case, extraction of the aromatic hydrocarbons was carried out in glass columns filled with ASK-100 silica gel, which was first dried at 150-155°, over a period of 5 hours. Removal of the paraffinic and naphthenic hydrocarbons from the surface of the adsorbent was accomplished with isopentane, and the aromatics were eluted with methanol. The isopentane was distilled from the fractions on a water bath in a stream of CO_2.

Deviations in the values of the aniline point, $T_{2(max)}$, determined after dearomatization of the fractions by either method, were in the range of 0-0.6° (Table 1).

TABLE 1

Group Chemical Composition of the Fractions

Fraction No.	Boiling range, °C	Yield based on petroleum, %	d_4^{20}		n_D^{20}		$T_{(max)}$		Content of hydrocarbon types, wt. %*			
			Orig.	Dearomat.	Orig.	Dearomat.	Orig.	Dearomat.	Aromatic	Paraffinic	Naphthenes	
											total	six-membered
	I. b. p.	2.7										
I	60-95	5.1	0.7113	0.7034	1.4109	1.4045	49.9	57.2	8.4 8.8	53.1 56.5	38.5 34.7	15.7
II	95-122	4.7	0.7461	0.7303	1.4189	1.4108	48.6	60.2	13.9 14.1	50.0 51.6	36.1 34.3	16.7
III	122-150	4.9	0.7639	0.7489	1.4278	1.4163	50.8	64.1	16.8 17.3	50.0 49.9	33.2 32.8	7.2
IV	150-200	9.9	0.7882	0.7685	1.4381	1.4267	56.2	70.6	21.6 20.6	50.9 54.4	27.5 25.0	

* Above line – calculated by GrozNII aniline coefficient [1]; under line – calculated by the coefficient proposed by P. S. Maslovyi and V. I. Konoplina.

A high (of the order of 50%) content of paraffinic hydrocarbons characterized all of the gasoline fractions. The content of aromatics was also rather considerable, and it increased on going from the lower to the higher. The naphthene content slowly decreased with an increase in the boiling range of the fractions. Cyclopentanes predominated among the naphthenes. Cyclohexanes comprised less than half of the total naphthenes of Fractions I and II and a small part of Fraction III (providing gem-substituted cyclohexanes were not present in significant amount). The data on the content of cyclohexanes were obtained by catalytic dehydrogenation of the dearomatized fractions by the method of N. D. Zelinskii at 300 ± 5° over a catalyst of 20% Pt and 2% Fe on carbon [2].

TABLE 2

Catalytic Dehydrogenation of the Gasoline Fractions

Fraction No.	Boiling range, °C	n_D^{20}			T			Content of hexahydro-aromatics, %	
		original	dehydro-genated	dearoma-tized	original	dehydro-genated	dearoma-tized	original	dearomatized
I	60-95	1.4045	1.4110	1.3980	57.2	49.0	63.0	15.7	17.3
II	95-122	1.4108	1.4200	1.4090	60.2	53.5	68.0	16.7	19.1
III	122-150	1.4173	1.4215	1.4135	65.0	62.8	69.4	7.2	9.1

The complete data from the catalytic dehydrogenation experiments are presented in Table 2.

According to the group chemical composition, the gasoline from Makhachkalin petroleum from well No. 92 is a mixed paraffinic-naphthenic-aromatic type. In comparison with other Daghestan petroleums, it contains a higher percentage of aromatic hydrocarbons.

TABLE 3

Individual Hydrocarbons in the Gasoline Fractions (by Raman Spectroscopy)

Hydrocarbon	B. p., °C	Content, vol. %	
		in 60-97° fraction	in petroleum
2-Methylpentane	60.27		
3-Methylpentane	63.28	6.5-7.8	0.64-0.77
n-Hexane	68.74	16.7-17.8	1.65-1.76
Methylcyclopentane	71.81	3.6-4.9	0.36-0.49
2,2-Dimethylpentane	79.20	1.8-2.4	0.18-0.24
2,4-Dimethylpentane	80.50	1.8-2.4	0.18-0.24
Cyclohexane	80.74	3.0-3.6	0.30-0.36
2,2,3-Trimethylbutane	80.87	to 0.3	to 0.03
3,3-Dimethylpentane	86.07	trace	trace
1,1-Dimethylcyclopentane	87.85	1.2-1.8	0.12-0.18
2-Methylhexane	90.05	4.4-5.1	0.44-0.50
Trans-1,3-dimethylcyclopentane	90.77		
Cis-1,3-dimethylcyclopentane	91.72	9.8-10.1	0.97-1.0
Trans-1,2-dimethylcyclopentane	91.87	4.7-5.4	0.47-0.53
3-Ethylpentane	93.98	to 0.6	to 0.06
n-Heptane	98.43	9.4	0.93
Cis-1,2-dimethylcyclopentane	99.53	trace	trace
Methylcyclohexane	100.93	6.9-7.5	0.68-0.74
	Total	70.7-79.1	7.01-7.85

Individual chemical composition. In order to obtain the qualitative characteristics of the individual chemical composition, the gasoline was dearomatized and distilled into 60-95° and 95-122° fractions in a column (26 theoretical plates). Narrow (1-5°) cuts, taken in the 60-97° range, comprised 10.1% of the petroleum. Equivalently boiling distillates which were close in physical properties were combined and subjected to analysis by Raman spectra.

The spectra were photographed in an ISP-51 3-prism glass spectrograph with a f/270-mm camera. The exciting radiation was the 4358 A mercury line, which was filtered with a saturated solution of sodium nitrite. Quantitative evaluation was carried out by the standard photographic method [3] of comparing the intensity of the line of a given component with the intensity of the line of a standard material, for which methylcyclohexane was used.

As a result of the investigation of 60-97° fractions, 18 individual hydrocarbons were determined (Table 3). Among them were two normal paraffins, eight isoparaffins, two hydrocarbons of the cyclohexane series, and six cyclopentanes. These hydrocarbons comprised approximately 71-79% of the fraction. Accurate contents of the individual hydrocarbons and the ratios between groups could not be determined, since certain lines of the fractions were not decipherable and narrow fractions were not analyzed. Thus, owing to the small volume, the following fractions were not studied: 70-73°, 73-75°, and 82-87°. Owing to this, the amount of cyclohexane, for example, is obviously somewhat minimized. The same should be noted in connection with n-heptane and methylcyclohexane, which partially fell into the given fraction and had to be distilled with the higher boiling.

Nevertheless, the results obtained permit us to consider without doubt, that the individual chemical composition of Makhachkalin gasoline is a typical mixed type in which paraffinic hydrocarbons predominate over naphthenic.

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CHLORINATION OF DIACETYLENE SYNTHESIS OF HEXACHLORO-1,3-HEXADIENE

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(Presented by Academician A. V. Topchiev, August 2, 1958)

The halogenation of diacetylene has been well studied with respect to the additon of bromine [1]. There are no corresponding data for chlorination in the literature.

In the present communication is described a method developed by us for the chlorination of diacetylene in a medium of carbon tetrachloride at a temperature of −30 to −25°. The reaction proceeded with the formation of liquid and crystalline 1,1,2,3,4,4-hexachloro-2-butene. Müller and Hüther [2] reported on the geometrical isomers of 1,1,2,3,4,4-hexachloro-2-butene, both liquid and crystalline. These isomers were isolated by them during an investigation of butane halogen compounds formed as by-products during the manufacture of trichloroethylene. The authors indicated that hexachlorobutenes do not react with chlorine or bromine.

We were able to carry out the further chlorination of hexachlorobutenes with liquid chlorine under pressure and with ultraviolet irradiation. With a large excess of chlorine (4-8 and more moles), chlorinolysis was not observed, and octachlorobutane was obtained in quantitative yield. Subsequent dehydrochlorination of octachlorobutane gave hexachloro-1,3-butadiene – a product possessing a number of valuable technical properties. The patent literature [3] described a method for the production of hexachlorobutadiene from octachlorobutane (obtained from other starting materials by a route involving more steps). Another patent [4] describes a continuous process for the production of hexachlorobutadiene based on hexachlorobutene and chlorine. Syntheses of hexachlorobutadiene from heptachlorobutene have been described [5, 6]. It is obtained by chlorination of polychloropentanes at high temperature and normal pressures [7].

It should be noted that the patent recommends splitting out HCl from octachlorobutane by boiling with alcoholic alkali. We are convinced that this considerably contaminates the hexachlorobutadiene with by-products of the reaction, because it is not inert under the indicated conditions. In fact, it has been shown comparatively recently [8] that on boiling with alcoholic alkali, hexachlorobutadiene reacts by substituting an alkoxy group for chlorine with the formation of perchlorinated vinyl and orthoesters. Therefore, we carried out the dehydrochlorination of octachlorobutane with aqueous-alcoholic alkali at a temperature not exceeding 30°.

EXPERIMENTAL

The diacetylene was prepared by a well-known method, somewhat modified in our laboratory and described previously [9].

1. The chlorination of the diacetylene was carried out in an apparatus with a mechanical stirrer. Dry chlorine was passed into 100 ml of carbon tetrachloride, cooled to −50°, until the required weight increase was obtained (calculated as a 2-3 fold excess). While stirring vigorously, the diacetylene was carried from a trap into the reaction flask by a uniform stream of nitrogen. For a period of 5-6 hours, the temperature of the experiment was maintained at −30 to −25°, and the mixture was allowed to stand overnight with cooling. After removal of the chlorine and solvent, the reaction mixture was separated into liquid and crystalline parts by pressing on a glass filter. The results of some experiments are presented below (Table 1).

TABLE 1

Chlorination of Diacetylene

Expt. No.	Diacetylene, g	Chlorine, moles per mole of diacetylene	Yield of reaction products, %			Note
			crystalline	liquid	total	
4	6	3.1	63	19	82	Total duration of all experiments was 25-30 hours
8	5.6	2.7	56.5	23.8	80.3	
10	6.6	4.2	60.3	18.7	79	
13	6.8	3.4	47.6	25.2	72.8	
16	5.7	4.1	58.5	15	73.5	

As seen from the data of Table 1, the over-all yield of reaction products varied from 73 to 80%, and there was no direct dependence on the initial concentration of chlorination. This same variation occurred in the yields of crystalline and liquid fractions (15-25%). This is understandable if it is remembered that the crystalline isomer is rather soluble in the liquid.

Experiment 4. Upon removal of the chlorine and solvent from the reaction mixture, there remained 28 g of a white, crystalline product. Pressing on a glass filter gave 19.9 g of dry crystals and 6 g of mother liquor. After one recrystallization from boiling ethanol, the crystals melted at 78°, and analysis of the mixture agreed with hexachloro-2-butene.

Found %: C 18.69, 18.55; H 1.00, 0.92; Cl 80.39, 80.49. $C_4H_2Cl_6$. Calculated %: C 18.28; H 0.77; Cl 80.95.

The literature gives a m. p. of 80° [2]. An additional small portion of the crystalline isomer settled out on storage of the liquid. The liquid portions from all experiments were combined, fractionated under vacuum, and subjected to further chlorination (see Part 2b). A broad fraction, 82-90°/4mm, was usually used.

2. Synthesis of octachlorobutane. A weighed portion of hexachlorobutene, dissolved in carbon tetrachloride, was placed in a tube with an inlet. Upon the addition of the required amount of chlorine (4-8 molar excess), the tube was sealed. The contents of the tube were carefully agitated, and, while in a horizontal position, the tube was irradiated with a quartz lamp (20-25 hours). At the conclusion of the reaction (3-4 days), the tube was frozen and opened; the excess chlorine was vaporized, and the reaction mixture was transferred to a distillation apparatus for removal of the residual chlorine and solvent.

a) Chlorination of crystalline 1,1,2,3,4,4-hexachloro-2-butene. Experiment 14. 25 g of hexachlorobutene (m. p. 78°) in 100 ml of CCl_4 and 65 g of liquid chlorine were sealed in a tube. The weight of the crystalline reaction product was 32 g. The first crystallization from boiling alcohol gave 25 g of a substance with a m. p. of 79.5°. A mixture of a sample with known hexachlorobutene melted at 52-55°; i.e., there was a sharp depression; as analysis showed, the synthesized substance was octachlorobutane.

Found %: C 14.14, 14.08; H 0.69, 0.49; Cl 85.42, 85.23. $C_4H_2Cl_8$. Calculated %: C 14.40; H 0.60; Cl 85.00.

The literature [3] gives a m. p. of 81°. From the mother liquor of the first crystallization was isolated another 4 g of crystals with a m. p. of 79°; a mixture with the major product did not show a m.p. depression. Thus 29 g (91% of theoretical) of crystalline octachlorobutane was isolated.

b) Chlorination of liquid 1,1,2,3,4,4-hexachloro-2-butene. Experiment 30. 15 g of the liquid isomer (b. p. 82-90°/4 mm) in 50 ml of CCl_4 and 31 g of liquid chlorine were sealed in a tube. The weight increase of the reaction mass was 4 g. After two crystallizations from boiling alcohol, 13.9 g (76% of theoretical) of a crystalline material melting at 79° was isolated; a mixture of this material with known octachlorobutane, synthesized from the crystalline isomer, showed no m. p. depression. Fifteen such experiments were carried out. The combined, decanted mother liquors gave, besides additional crystalline material, a thick, uncrystallizable oil. We did not undertake a detailed investigation of this product.

3. Synthesis of hexachlorobutadiene. 20 g of octachlorobutane in 200 ml of alcohol were placed in the flask of an apparatus fitted with a mechanical stirrer. With vigorous stirring, an aqueous-alcoholic 1 N solution of NaOH was added to the appearance of a stable rose color of the reaction mixture containing phenolphthalein; during this, the temperature rose from 20 to 32-34°. Stirring was continued at 30° for 1-1.5 hours, and the mixture was filtered from the precipitated sodium chloride. The alcohol was removed from the filtrate under vacuum, and, after dilution with water, the reaction product was separated, diluted with a very small amount of ether, and dried with calcium chloride. Vacuum distillation gave 10.4 g (67%) of hexachlorobutadiene – an oily colorless liquid with an agreeable turpentine odor – which had the following constants: b. p. 214°/755 mm, 57.5-58°/2 mm, 58-60°/2.5 mm, n_D^{20} 1.5540; 1.5542.

Found %: C 18.67, 18.79; Cl 81.38, 81.24. C_4Cl_6. Calculated %: C 18.42; Cl 81.58.

Literature data: m.p. −21°, b. p. 215°/760 mm, n_D^{20} 1.5542, d_4^{20} 1.6820 [5, 7]; 210°/760 mm, 64-65°/0.5 mm, n_D^{20} 1.5531 [6].

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INVESTIGATION OF THALLIUM DICHROMATE AND ITS USE IN QUANTITATIVE ANALYSIS

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(Presented by Academician I. I. Cherniaev, August 13, 1957)

Literature data on thallium dichromate is very limited and belongs mainly to the last century [1-5].

As early as 1867, Carstanjen [5] put forth the opinion that difficultly soluble compounds of thallium – its mono- and dichromates – could be used for the quantitative determination of this metal. Actually, the best method for the gravimetric determination of thallium, as recognized by a number of authors [6-8], is to determine it as the chromate [9].

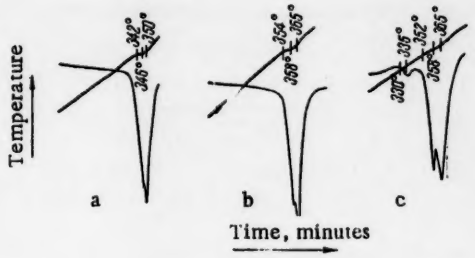

Fig. 1. Heating curves for thallium dichromate: a) unwashed; b) washed with acetone (washing with ethyl alcohol gives the same curve); c) washed with water and then with acetone.

Thallium has not been determined as the dichromate by anyone. Moreover, this compound is considered [10] unsatisfactory for the gravimetric determination of thallium. Precipitation of it from a solution of perchloric acid under strictly controlled conditions has been used analytically only for the separation of thallium (I) from thallium (III) and Fe [10]. However, the determination of thallium as the dichromate by precipitation from acid solutions is of undoubted interest, since this opens up the possibility of carrying out the determination of thallium while simultaneously separating it from associated elements. This advantage of the method is especially valuable for thallium – a metal which belongs to a group of widely scattered metals.

During an investigation of the water–salt systems formed by thallium chromate and chromic oxide and by thallium sulfate and chromic oxide, we established particularly that thallium dichromate is an incrogruently soluble compound, completely precipitated from solution by an excess of chromic oxide. This served as a theoretical basis for the development of a method for the quantitative determination of thallium as the dichromate.

In order to use thallium dichromate in gravimetric analysis as the compound to be weighed, it was necessary to find conditions for its quantitative separation from the mother liquor while retaining its composition.

In particular, it was established that thallium dichromate is insoluble in acetone and ethyl alcohol.

Phase differential thermal analysis was used to investigate thallium dichromate after washing it with the indicated solvents. The heating curves, obtained with a Kurnakov pyrometer, are presented in Fig. 1. The first two of these curves (Fig. 1a and b), which refer, respectively, to thallium dichromate well separated from the mother liquor by filtration and thallium dichromate washed with acetone (or ethyl alcohol), are similar. They are characterized by two endothermic effects. Visual observation of these effects showed that the first of them corresponded to the appearance of a liquid phase, and the second corresponds to complete melting of the salt. The temperature of the heat effects differed somewhat on the two thermograms. Naturally, they were lower on

on the heating curve for the unwashed thallium dichromate, which contained, consequently, a certain amount of the dry residue of the mother liquor.

The identical character of these thermograms indicates that thallium dichromate does not change composition during washing with acetone or ethyl alcohol.

TABLE 1

Determination of Thallium as the Dichromate

Expt. No.	Taken for the precipitation, g per 100 ml			Found* Tl_2SO_4, g	Error, mg
	Tl_2SO_4	CrO_3	H_2SO_4		
1	0.1000	0.25	—	0.0998	—0.2
2	0.1000	0.75	1	0.0998	—0.2
3	0.1000	0.75	10	0.0992	—0.8
3**	0.1000	0.75	10	0.0999	—0.1
4	0.1000	1.5	—	0.0999	—0.1
5	0.1000	1.5	10	0.0998	—0.2
5**	0.1000	1.5	10	0.1000	0.0
6	0.1000	2.25	18	0.0988	—1.2
6**	0.1000	2.25	18	0.0997	—0.3
7	0.1000	8.0	—	0.0998	—0.2

* Average value of several determinations.

** The thallium dichromate precipitate was allowed to stand with the mother liquor, the volume of which did not exceed 100 ml, for 2-4 hours at a temperature of 1-3°. In the remaining experiments, standing was for 18-20 hours at room temperature.

The heating curve of the thallium dichromate which was washed with water and only afterwards with acetone (Fig. 1c) is characterized by an additional endothermic effect, which occurred in the solid state and which corresponds to a polymorphic transformation of thallium chromate that was recorded thermographically during the heating. The presence of this effect indicates decomposition of the thallium dichromate, and, consequently, confirms the incongruent nature of its solution.

It is characteristic that the decomposition of thallium dichromate during the action of water on the chromate and chromic oxide proceeds very slowly. This is of separate interest, and is explained, most probably, by the poor solubility of thallium chromate and dichromate.

In order to determine the conditions for the quantitative determination of thallium as the dichromate, we carried out a systematic investigation of its precipitation by chromic oxide from neutral and acid (sulfuric and nitric) solutions and also of its precipitation by sodium, potassium, and ammonium dichromates.

The results of the determinations of thallium as the dichromate, certain of which are presented in Table 1, demonstrate the possibility of quantitatively determining thallium by this method, and, by the same token, they controvert the contradictory assertions in the literature [10].

These results permitted us to determine the dependence of the average error in the determination of thallium, by precipitation from sulfuric acid solutions with chromic oxide, on the different ratios of these components in the solution. This relationship made it possible to determine the permissible range of concentrations of the indicated components in the quantitative precipitation of thallium, and to establish the optimum conditions for the determination of thallium.

A comparison of the results of the analyses carried out with cooling of the solution containing potassium dichromate precipitate with those of analyses carried out at room temperature shows (Table 1) that in the first case quantitative results were obtained, while in the other case, in which there was no cooling, the results were not quantitative.

Determination of thallium as the dichromate permits wide variation both in the concentration of acid in the solution and in the concentration of the dichromate precipitant. These experimental data makes it possible to determine, in each particular case, the concentration of chromic oxide, required for the quantitative precipitation of the thallium, with respect to the concentration of acid in the solution.

In the general case of the quantitative determination of thallium, it is expedient to precipitate it as the dichromate from solutions containing up to 10 g of H_2SO_4 (or HNO_3) in 100 ml of solution using an average concentration of chromic oxide (or sodium dichromate) of 1 g in 100 ml of liquid phase.

When the thallium was precipitated with potassium or ammonium dichromate, the results of the determinations were too high; they were satisfactory only in certain cases.

As we were able to show, the determination of thallium as the dichromate can be carried out not only by the gravimetric method, but also by an indirect volumetric method based on the amount of precipitant reacted.

One of the variations of the method might be the radiometric determination of thallium as the dichromate using the radioactive isotope Tl^{204}.

TABLE 2

Determination of Thallium as the Dichromate in the Presence of Other Metals

Expt. No.	Tl_2SO_4 used, g	Present	$TlSO_4$ found, g	Error, mg
1**	0.1000	Sulfates* Zn, Cd, Al, Fe(III), Cu(II) up to 1 g		
		Ni, Co up to 0.5 g	0.0999	−0.1
		In, Ga, Ge 0.1 g	0.1000	0.0
2**	0.1000	Nitrates:	0.0997	−0.3
		Ag, Bi, Hg(II) up to 0.01 g	0.1000	0.0
3***	0.1000	Nitrates		
		Pb, Bi up to 0.02 g	0.0999	−0.1
		Ag, Hg(II) up to 0.01 g	0.1002	+0.2
		Ba 0.1 g		
4**	0.1000	All salts indicated for Nos. 1 and 2 in the	0.0997	−0.3
		same amounts	0.0999	−0.1

* The amount of sulfates is given without water of crystallization.
** Precipitation carried out from sulfuric acid solution.
*** Precipitation carried out from nitric acid solution.

The proposed new method for the quantitative determination of thallium has a number of advantages over known methods of determination. Along with the others the basic advantage is the possibility of determining thallium without first separating the basic accompanying elements. This possibility was borne out by the results of determinations of thallium by precipitation as the dichromate from acid solutions containing other metals. Some of these data are presented in Table 2.

The results showed that the direct determination of thallium as the dichromate is possible in the presence of metals, irrespective of their concentration, which do not form insoluble compounds under the conditions of the analysis. In addition to the metals indicated in Table 2, satisfactory results were also obtained in the presence of Tl (III), Fe (II), Cr (III), and Sb (III). Naturally, the number of such metals can be considerably increased.

The determination of thallium as the dichromate is also possible in the presence of small amounts of metals which precipitate as chromates (Table 2, Nos. 2 and 3). The limiting permissible concentrations were established for this group of metals.

Thus, it was shown that the quantitative determination of thallium as the dichromate is simultaneously a method for its separation from associated elements, which solves this complex problem in a simple and practicable manner.

The determination of thallium as the dichromate may be used for analyses of various intermediate products in industrial production and for all other materials containing thallium. The feasibility of quantitatively separating thallium from associated elements by quantitative precipitation as the dichromate, in addition to analytical applications, has considerably wider prospects for use.

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SYNTHESIS OF ETHANOL FROM CARBON DIOXIDE AND HYDROGEN

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(Presented by Academician A. V. Topchiev, July 12, 1957)

The catalytic hydrogenation of carbon dioxide with hydrogen at normal pressure usually leads to the formation of hydrocarbons and carbon monoxide. Methane is the chief product of the reduction; the yield of liquid hydrocarbons comprises 20-40 g per cu. m. of feed gas at a $CO_2:H_2$ ratio of 1:3 [1-5].

TABLE 1

Effect of Various Process Variables on Product Composition

Temperature, °C	Pressure, atm.	Space rate, liters/liter·hour	$CO_2:H_2$ in feed gas	Alcohol content in condensate, wt. %	Fractional composition of alcohols, wt. %		
					Up 72°	72–82°	82–94°
335	200	300	1:3	21.3	60.8	22.3	16.9
350	200	300	1:3	16.6	16.9	74.6	8.5
370	200	300	1:3	12.2	20.5	45.2	34.3
350	200	300	1:3	16.6	16.9	74.6	8.5
350	250	300	1:3	12.5	46.6	36.2	17.2
350	300	300	1:3	13.7	53.3	30.7	16.0
350	350	300	1:3	14.7	59.8	25.6	14.6
350	400	300	1:3	10.8	66.6	33.4	0
350	200	300	1:1.7	10.8	32.4	50.2	20.4
350	200	300	1:3	16.6	16.9	74.6	8.5
350	200	300	1:20	6.8	6.7	68.2	25.1

Carrying out the process with the CO_2 and H_2 under pressure and over oxide catalysts leads chiefly to the formation of methanol [6-8]. Along with the methanol, depending on process conditions and catalyst composition, a certain amount of higher alcohols (ethanol, propanol, butanol, etc.) is formed [9, 10]. This provided us with a basis for conducting an investigation having as its aim the accomplishment of the directed synthesis of ethanol from CO_2 and H_2. A large number of different catalysts was tested for this purpose, and the effects of various variables (pressure, temperature, feed gas composition, etc.) on the synthesis process were studied.

The synthesis was carried out in a high-pressure apparatus which has been repeatedly described in our previous communications [11]. When operating under recycle conditions, the effluent gas was returned to the synthesis by a circulating pump. Fresh gas was fed directly into the reactor.

Prior to use in the synthesis, the catalysts were reduced with hydrogen. The synthesis products were subjected to analysis. The aqueous condensate from the receiver, a colorless, slightly turbid liquid with traces of oil, was fractionated in a highly efficient column into methyl, ethyl, and propyl alcohol fractions. Butyl and higher alcohols were present in very small amounts. The effluent gas was passed through a carbon adsorber, in which hydrocarbons and volatile oxygen-containing products were collected. After desorption, the reaction products were analyzed.

Various precipitated catalysts based on iron, cobalt, and nickel as well as fused iron catalysts (ammonia-synthesis type catalyst) promoted with various promoters (K_2O, Al_2O_3, SiO_2, MnO, etc.) were tested.

The most effective were the alkaline promoters, which were introduced during fusion of the catalyst or by impregnation with an aqueous solution of the alkali. The fused iron catalysts possessed higher stability and selectivity than the precipitated catalysts. In Table 1 are presented the results of certain experiments showing the effect of temperature, pressure, and feed gas composition on product composition.

The condensate obtained during the synthesis from CO_2 and H_2 over one of the fused iron catalysts was subjected to a more detailed investigation. During a run of more than 2500 hours, the catalyst activity and product composition remained practically constant.

Properties of the condensate were: d_4^{20} 0.9701, acid number 9.2, ester number 0, carbonyl number 2.1.

The alcohol fraction (up to 94°) obtained by fractionation was treated with potassium hydroxide and silver nitrate, and, after drying over metallic potassium, was distilled on a highly efficient column.

Distillation results:

		g	%
Amount		371.4	
Initial b. p. 62°			
Fraction:	62.5-65.0	40.2	10.8
	65.0-77.0	7.8	2.1
	77.0-79.0	279.6	76.3
	79.0-96.5	6.3	1.7
	96.5-98.0	20.8	5.6
Residue		13.4	3.6
Loss		3.3	0.9

The resulting fractions of methyl, ethyl, and propyl alcohols were distilled again, fractions with a boiling range of 0.2-0.3° and corresponding to methanol, ethanol, and propanol being collected.

TABLE 2

Results of the Investigation of the Alcohols

Alcohol	d_4^{20}		B. p., °C		n_D^{20}		Hydroxyl Hydroxyl number		M.p. of phenylurethan, °C	
	found	literature value	found	literature value	found	literature value	found	calc.	found	literature value
Methanol	0.7947	0.7942	64.3	64.56	1.3286	1 32857	1733	1751	47—48*	47
Ethanol	0.7899	0.7893	78.2	78.33	1.36125	1.36127	1215	1218	51—52*	52
n-Propanol	0.8055	0.8044	97.5	97.22	1.3848	1.38543	926	934	50.3—51.3*	51

* Mixed samples of phenylurethans of the alcohols obtained with phenylurethans of known corresponding alcohols showed no m. p. depression.

The cited results show that the major alcohol product obtained by the catalytic reduction of carbon dioxide was ethyl alcohol.

Along with the alcohols, acids amounting to about 1% of the condensate were obtained. An investigation showed that the major part (more than 90%) of the acids was acetic acid. The silver content of the silver salt of the isolated acid was 64.7; calculated for acetic acid 64.64%.

The product desorbed from the activated carbon was also investigated (see Tables 3 and 4).

The liquid desorption product, which we nominally designate as gas gasoline, had d_4^{20} 0.7052, n_D^{20} 1.3933, iodine number 103.9. Analysis of the gaseous desorption product was by low-temperature fractionation (Table 4).

TABLE 3

Distillation of Gas Gasoline (72.0 g taken for the distillation)

Boiling range, °C	d_4^{20}	n_D^{20}	Iodine number	Yield	
				g	%
Up to 90	0.6785	1.3810	124.8	38.31	53.2
90—122	0.7407	1.3971	80.8	21.27	29.5
122—150	0.7703	1.4075	65.1	8.25	11.5
150—200	0.7662	1.4150	55.9	1.51	2.1
Residue					
Residue and loss	—	—	—	2.66	3.7

TABLE 4

Low-Temperature Distillation Results

Empirical formula of the chemical compound	Content	
	vol. %	wt. %
H_2	3.0	0.2
CH_4	11.6	4.8
C_2H_4	1.1	0.8
C_2H_6	24.3	19.0
C_3H_6	5.7	6.2
C_3H_8	39.4	45.2
iso-C_4H_8	0.1	0.2
iso-C_4H_8	1.8	2.6
iso-C_4H_{10}	1.3	2.0
n-C_4H_{10}	7.8	11.7
Residue	3.9	7.3
	100	100

TABLE 5

Effect of Space Rate on Alcohol Content of Condensate (temperature 335°, pressure 200 atm., feed gas $CO_2 : H_2 = 1 : 3$)

In flow content		With recycle	
Space rate, liters/liter/hour	alcohol content of condensate, wt. %	Space rate, liters/liter/hour	alcohol content of condensate, wt. %
300	21.3	600	20.5
600	16.8	3 400	19.4
7 200	9.6	8 000	18.1
30 400	7.2	20 800	16.6
70 500	5.0	57 200	12.3
145 000	3.2	109 000	6.4
197 000	1.4	142 000	5.8

In the course of the investigations, some data were obtained relative to the chemism of the catalytic reduction of carbon dioxide under pressure. An essential feature of this process is that it is a step process. The interaction of carbon dioxide with hydrogen in the initial step leads to the formation of carbon monoxide in concentrations not exceeding the equilibrium concentration of the water gas reaction.

The resulting carbon monoxide is the basic source of the formation of oxygen-containing compounds and hydrocarbons. With an increase in the concentration of water vapor in the reaction mixture, the equilibrium concentration of carbon monoxide decreases, and the synthesis practically ceases when the carbon monoxide concentration reaches about 2%. When the synthesis is carried out in a flow system, such a state is reached at a feed gas conversion of about 50%. At high space rates and, consequently, low contact time, carbon monoxide is the major product of the reduction of carbon dioxide. For illustration, we present data on the effect of space rate on the formation of carbon monoxide (temperature 350°, pressure 200 atm., feed gas $CO_2 : H_2 = 1 : 3$):

Space rate, liters/liter/hour	Fraction of CO_2 converted to carbon monoxide, % of CO_2 reacted
6600	20.2
8200	33.2
17200	40.0
81000	53.0
148000	65.0
246000	94.5

The data presented show that carrying out the synthesis with CO_2 and H_2 in a flow system at high space rates is coupled with the formation of considerable amounts of carbon monoxide.

Carrying out this synthesis under recycle conditions permits, even at space rates up to 20,000 liters/liter/hour, supression of the formation of carbon monoxide to a considerable extent. In Table 5 are presented some data on the composition of the products obtained during synthesis from CO_2 and H_2 in a flow system with recycle.

This investigation permitted us to carry out an approximate material balance over the basic synthesis products.

The yield per cu. m. of gas used ($CO_2 : H_2 = 1 : 3$) was (in grams):

Alcohols	92	Carbon monoxide	31
Hydrocarbons	81	Other oxygen-containing	
Water	345	compounds	10

It should be mentioned that the yield of acids (mainly acetic) increased with a decrease in contact time. A change in the space rate from 6,000 to 25,000 liters/liter/hour decreased the ratio of alcohols to acids by more than a factor of 20. This circumstance can be considered as an argument in support of the idea that the major product – ethyl alcohol – is formed by reduction of acetic acid.

From these investigations, a catalyst and synthesis conditions were found for the production of ethyl alcohol in high yield (about 90 g per cu. m. of feed gas with $CO_2 : H_2 = 1 : 3$). The best results were obtained when the process was operated with recycle of the effluent gas, a space rate of 10,000-20,000 liters/liter/hour, a temperature of 325-350°, and a pressure of 200 atm.

This new process for the synthesis of ethyl alcohol from carbon dioxide and hydrogen is of considerable interest, and is a step forward in the development of the still scant methods of processing carbon dioxide into valuable chemical products.

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DIRECT SYNTHESIS OF 4-SUBSTITUTED SALTS OF 1-AZADEHYDROQUINOLIZINE

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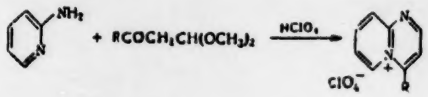
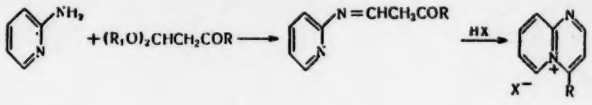
We recently published a method for the synthesis of salts of 4-alkyl-1-azadehydroquinolizine [1], which was based on the condensation of α-aminopyridine with acetals of acylacetaldehydes [2] and subsequent cyclization of the resulting condensation products by means of concentrated acids (HBr, $HClO_4$)



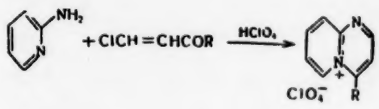
where R = Alk; R' = OCH_3-, OC_2H_5-; X = Br^-, ClO_4^-.

In the present work, we have considerably simplified the method, showing that these same compounds are formed by the direct condensation of β-chlorovinyl ketones with α-aminopyridine under the influence of 70% perchloric acid.



where R = CH_3-, C_3H_7-, C_6H_5-.

Acetals of acetaldehyde, readily obtainable from β-chlorovinyl ketones [2], enter into this type of reaction; ring closure into a heterocycle, with the same results:



where R = CH_3-, C_3H_7-, C_6H_5-.

This variant of the method has an independent significance, since the first homolog of the series of acetals of acylacetaldehydes – the acetal of acetaldehyde – has recently become a technical product readily obtainable from diacetylene, and syntheses based on it have acquired practical value [3, 4].

This method of synthesis also opened up the possibility of obtaining the perchlorate of 4-phenyl-1-azadehydroquinolizine.

The structures of the salts obtained were demonstrated in a previous communication [1]. Possible 2-substituted isomers, the formation of which might be expected, were not found in either case.

EXPERIMENTAL

1. Perchlorate of 4-methyl-1-azadehydroquinolizine [1]. a) To a mixture of 2 g of α-aminopyridine and 2 g of methyl-β-chlorovinyl ketone in 5 ml of absolute methyl alcohol was added 4 ml of 70% perchloric acid. There was considerable evolution of heat. After a day, the resulting precipitate was filtered, and an additional small amount of the salt was precipitated with ether from the mother liquor. The yield of 4-methyl-1-azadehydroquinolizine perchlorate was 3.9 g (75% of theoretical), decomposition temperature 224-226° (from methanol).

b) The material was similarly prepared from 3 g of the dimethyl acetal of acetoacetaldehyde, 2 g of α-aminopyridine, and 3.5 ml of 70% perchloric acid in 5 ml of absolute methyl alcohol. The yield was 3.65 g (72% of theoretical), decomposition temperature 223-226°. A mixture with a known sample and with a sample of the material prepared by variant (a) showed no melting point depression.

2. Perchlorate of 4-propyl-1-azadehydroquinolizine [1]. a) This compound was prepared similarly from 1.5 g of propyl-β-chlorovinyl ketone, 1 g of α-aminopyridine, and 2 ml of 70% perchloric acid in 2.5 ml of absolute methyl alcohol. In cases where the salt did not precipitate on long standing, it was necessary to precipitate it from the solution with ether. The yield was 2.5 g (82% of theoretical), m. p. 143-145° with decomposition (recrystallized from absolute methyl alcohol).

b) The compound was prepared similarly from 1.8 g of the dimethyl acetal of propionacetaldehyde, 1 g of α-aminopyridine, 1.7 ml of 70% perchloric acid in 2.5 ml of methyl alcohol. The yield of 1.75 g (60.3% of theoretical), m. p. 144-145° with decomposition. A mixture with a known sample of the material prepared by variant (a) showed no m. p. depression.

3. Perchlorate of 4-phenyl-1-azadehydroquinolizine. a) The compound was prepared from 1.77 g of phenyl-β-chlorovinyl ketone, 1 g of α-aminopyridine, and 2 ml of 70% perchloric acid in 3 ml of absolute methyl alcohol. When the material did not precipitate, it was precipitated from the solution with ether. The precipitate was a mixture of 4-phenyl-1-azadehydroquinolizine perchlorate and tribenzoylbenzene. The 4-phenyl-1-azadehydroquinolizine perchlorate was separated from the tribenzoylbenzene by fractional crystallization from methyl alcohol. The yield of 4-phenyl-1-azadehydroquinolizine perchlorate was 0.35 g (10.8% of theoretical). Decomposition temperature 188-189°. The colorless, lamellar crystals were difficultly soluble in water.

Found %: C 54.82, 55.02; H 3.67, 3.64; Cl 11.58, 12.00. $C_{14}H_{11}O_4N_2Cl$. Calculated %: C 54.81; H 3.58; Cl 11.58.

b) The compound was also prepared from 2 g of the dimethyl acetal of benzoylacetaldehyde, 1 g of α-aminopyridine, and 1.7 ml of 70% perchloric acid. The yield of 0.45 g (12.7% of theoretical). Decomposition temperature 187-188°. A mixture with a sample of the material prepared by variant (a) showed no m. p. depression.

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REDUCTION OF MONOOLEFINIC HYDROCARBONS BY SODIUM IN LIQUID AMMONIA IN THE PRESENCE OF TERTIARY BUTYL ALCOHOL

M. I. Rozhkova, I. V. Gostunskaia and Academician B. A. Kazanskii

As was reported earlier [1], the reduction of isolated carbon-carbon double bonds by alkali metals in liquid ammonia apparently proceeds by an ionic mechanism:

$$>C=C<+2\bar{e}\rightarrow>C\bar{e}-C\bar{e}< \quad (a)$$

$$>C\bar{e}-C\bar{e}<2H^{+}\rightarrow>CH-CH< \quad (b)$$

$$2\bar{e}+2H^{+}\rightarrow H^{2} \quad (c)$$

The overall reaction rate of the reduction is determined by the ratio of the rates of two concurrent reactions: the addition of hydrogen to the double bond of the olefin ((a) and (b)) and the liberation of free hydrogen (c). In turn, the rates of these reactions depend on the structure of the olefin, the nature of the metal, and the acidity of the protolytic agents.

In previous work [1], we studied the effect on the rate of reduction of the nature of the metal in the series Li, Na, K and the acidity of the alcohol using methyl and ethyl alcohols as examples. α-Monoolefinic hydrocarbons can be reduced by Na, K, and Li in liquid ammonia in the presence of methyl and ethyl alcohols, but hydrocarbons in which the double bond is removed from the end of the chain are not reduced under these conditions. Apparently, the effect of two electron-donor alkyl groups at the double bond is to hinder the formation of a carbanion, that is, to reduce the rate of Reaction (a), thereby increasing the relative rate of the reaction forming hydrogen from electrons and protons (Reaction (c)).

TABLE 1

Hydrocarbon	Per cent reduction		
	Na + NH₃ + CH₃OH	Na + NH₃ + C₂H₅OH	Na + NH₃ + tert-C₄H₉OH
1-Pentene	43	45	72
1-Hexene	40	42	60
1-Heptene	38	41	42
1-Octene	20	29	32
1-Nonene	6	20	16
1-Decene	4	8	8

Therefore, it seemed of interest to carry out the reduction of monoolefins having double bonds in different positions in the presence of a weaker source of protons than methyl or ethyl alcohols, thereby decreasing the rate of the side reaction. Tertiary butyl alcohol was chosen as the weak protolyte, its acidity, according to McEwen [2], being 10 times less than that of ethyl alcohol. Sodium served as the metal reducing agent. The following olefins of normal structure were subjected to reduction: 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 2-pentene, a mixture of 2-hexene and 3-hexene, 3-heptene, and 2-octene. A large number of the α-monoolefinic hydrocarbons studied was reduced by sodium in liquid ammonia in the presence of tertiary butyl alcohol more rapidly than under analogous conditions in the presence of methyl or ethyl alcohol, as is seen from the data of Table 1.

Under these same conditions, β- and γ-monoolefins are reduced to a very slight extent, but with some changes in the method of carrying out the reaction, the reduction proceeds at an appreciable rate: 2-pentene was reduced to the extent of 12%, the mixture of hexenes – 11%, the 3-pentene – 9%, the 2-octene – 5%.

Thus, a decrease in the relative rate of formation of free hydrogen through the use of a weaker protolytic agent permits reduction of even such hydrocarbons as β- and γ-olefins, normally inert toward reduction under these conditions.

It is characteristic that the rates of reduction of β- and γ-olefins of differing molecular weight differ but little; this is in contrast to the α-olefins, for which the relationship between rate of reduction and molecular weight is rather sharply expressed. Moreover, reduction of β- and γ-olefins proceeds at approximately the same rate; i.e., the position of the double bond inside the olefin chain has little effect on the reduction.

The data obtained serve as further confirmation of the ionic mechanism for the reduction of an isolated double bond by metals in liquid ammonia.

EXPERIMENTAL

The method of synthesis of the monoolefins has been described by us previously [1]. 2-Pentene (b.p. 36.6-36.8°/760 mm, n_D^{20} 1.3810, d_4^{20} 0.6502) was prepared by the reduction of piperylene with sodium in liquid ammonia in the presence of methyl alcohol; the mixture of 2-hexene and 3-hexene (b.p. 67.5-68.0°/760 mm, n_D^{20} 1.3930, d_4^{20} 0.6785) was prepared by catalytic hydrogenation of dipropylene over palladium. The constants of the α-monoolefins agreed with the most reliable literature values [3]. The constants of the β- and γ-olefins corresponded to those of a mixture of the cis- and trans-isomers. The bromine numbers of all of the monoolefins investigated were close to the theoretical values.

Properties of the monoolefins investigated. 1-Pentene: b.p. 30.0°/760 mm, n_D^{20} 1.3718, d_4^{20} 0.6411; 1-hexene: b. p. 63.2°/760 mm, n_D^{20} 1.3876, d_4^{20} 0.6735; 1-heptene; b. p. 93.7°/760 mm, n_D^{20} 1.3995, d_4^{20} 0.6965; 3-heptene: b.p. 95.7-95.8°/760 mm, n_D^{20} 1.4048, d_4^{20} 0.7002; 1-octene: b.p. 121.3°/760 mm, n_D^{20} 1.4092, d_4^{20} 0.7155; 2-octene: b.p. 124.7-125.2°/760 mm, n_D^{20} 1.4140, d_4^{20} 0.7215; 1-nonene: b.p. 146.6°/760 mm, n_D^{20} 1.4158, d_4^{20} 0.7292; 1-decene: b.p. 170.7°/760 mm, n_D^{20} 1.4215, d_4^{20} 0.7410.

TABLE 2

Hydrocarbon	n_D^{20}	Bromine number	H_2, mole %: added to $H_2C{=}CR_2$	H_2, mole %: liberated in the free state
1-Pentene	1.3615	63.5	72	33
1-Hexene	1.3799	76.0	60	30
1-Heptene	1.3947	95.2	42	21
1-Octene	1.4052	97.2	32	20
1-Nonene	1.4143	105.8	17	25
1-Decene	1 4208	106.0	8	32

Reduction of β- and γ-monoolefins. Reduction of 2-pentene, the mixture of 2-hexene and 3-hexene, 3-heptene, and 2-octane was carried out under the same conditions as used for the α-monoolefins. The change in bromine number under these conditions was insignificant. In succeeding experiments, 0.32 g-atom of sodium and 0.4 mole of alcohol were used for each 0.08 mole of hydrocarbon. The concentration of sodium in liquid ammonia was maintained the same: 0.32 g-atom of sodium dissolved in 250 ml of liquid ammonia. The results are presented in Table 3.

Reduction of α-monoolefins. The reduction of the α-monoolefins and the investigation of the reaction products were carried out by Method A previously described by us [1]. For each 0.1 mole of hydrocarbon 0.2 g-atom of sodium and 0.25 mole of tertiary butyl alcohol were used. The reaction time was 3 hours. The results of the experiments are presented in Table 2. As can be seen from these data, the liberation of free hydrogen proceeded rather slowly; during an experiment, hydrogen liberation was 20-30% of theoretical; the rate of reduction of the α-monoolefins changed markedly with a change in the molecular weight of the olefin.

TABLE 3

Hydrocarbon	n_D^{22}	Bromine number	H_2, mole %: added to $HR_2C{-}CR_2H$	H_2, mole %: liberated in the free state
2-Pentene	1.3801	201.5	12	40
2-Hexene +3-hexene	1.3914	170.1	11	31
3-Heptene	1.4032	148.3	1	28
2-Octene	1.4133	135.7	5	25

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A NEW METHOD OF SYNTHESIS OF INDOLES SUBSTITUTED IN THE BENZENE NUCLEUS

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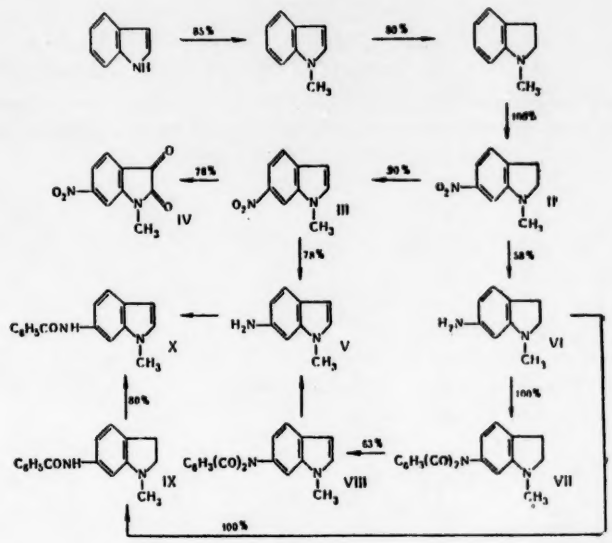
In connection with the discovery of serotonin and the search for antimetabolites for it, there have appeared a large number of investigations in the field of indoles substituted in the benzene nucleus. However, the synthesis of such indoles is very complex. The method of Reissert is ordinarily used, but this requires the use of a multi-step route starting from substituted o-nitrotoluenes which are frequently difficultly obtainable, and the resulting derivatives of α-indolylcarboxylic acids are usually decarboxylated with low yields. Synthesis by the Fischer method is hampered by the fact that many phenylhydrazines (for example, p-methoxyphenylhydrazine, etc.) and, especially, the corresponding hydrazones are very unstable. It has recently been found possible to introduce nitrophenylhydrazones of ketones into the Fischer reaction; however, cyclization of nitrophenylhydrazones of aldehydes to indoles proceeds with greater difficulty. A mixture of isomers is formed in the case of m-nitrophenylhydrazones. Synthesis of indoles from substituted anilines and α-bromoketones (Bischler method) leads to indoles containing substituents in the α- and β-positions as well as in the benzene nucleus. This method is used only in a limited number of cases for homologs of indole with aliphatic substituents. Indole itself cannot be prepared by this route.



The present work presents a new method for the synthesis of indoles substituted in the benzene ring. Indole (or a homolog of it) is reduced with the formation of an indoline, which is an aromatic amine, and substituents are introduced into the benzene ring by the usual reactions. The substituted indoline is dehydrogenated, and the corresponding substituted indole is obtained. It should be noted that both for the synthesis of derivatives of indole itself and of derivatives of its N- and β-substituted homologs the starting material is indole itself.

We prepared 6-nitro-1-methylindole, 6-amino-1-methylindole, and its benzoyl and phthalyl derivatives (see scheme on preceding page).

The methylation of indole and the preparation of 1-methylindoline, I, were carried out by a method described in the literature [1, 2]. The properties of I were very close to those of N,N-dimethyltoluidine. I was nitrated under conditions similar to those used for the nitration of dimethyltoluidine [3], and 6-nitro-1-methylindoline, II, was isolated. The dehydrogenation of II was carried out by refluxing in xylene with chloranil. (Julian and Printy dehydrogenated 1-methyl-5-methoxyindoline by a similar method [4]). The yield of 6-nitro-1-methylindole, III, was 61% calculated on the indole and 72% calculated on the 1-methylindole.

Oxidation of III with chromic acid gave nitromethylisatin, IV, which differed sharply in melting point from 5-nitro-1-methylisatin which is described in the literature [5]. Thus, the nitro group did not occupy the 5-position in our nitroindole. By analogy to the nitration of N,N-dimethyltoluidine and tetrahydroquinoline [6], we assume that our indole was 6-nitro-1-methylindole. Von Braun [7] also thinks that in the nitration of indoline derivatives, the nitro group enters the 6-position.

6-Amino-1-methylindole, V, was obtained by reduction of 6-nitro-1-methylindole with hydrazine hydrate in the presence of Raney nickel. The yield of V was 49% calculated on the indole.

6-Amino-1-methylindole was also prepared by another route. Reduction of 6-nitro-1-methylindoline, II, with stannous chloride gave 6-amino-1-methylindoline, VI. The properties of this material were very close to those of 1,1-dimethyl-m-phenylenediamine. Heating VI with phthalic anhydride gave 6-phthalimino-1-methylindoline, VII. The VII was dehydrogenated by refluxing in xylene with palladium black and cinnamic acid (see dehydrogenation of indoline [8]). On heating with hydrazine hydrate, the 6-phthalimino-1-methylindole gave 6-amino-1-methylindole, V. The benzoyl derivative prepared from the V obtained from 6-nitro-1-methylindole, III, and that prepared from the V obtained from 6-phthalimino-1-methylindole were identical (no mixed melting point depression). 6-Benzoylamino-1-methylindole, X, was also prepared by dehydrogenation of 6-benzoylamino-1-methylindoline. Dehydrogenation with chloranil in boiling xylene gave X with a yield of 80%, and dehydrogenation with palladium black and cinnamic acid gave a yield of 67%.

EXPERIMENTAL

6-Nitro-1-methylindoline, II. 28.9 g of 1-methylindoline, I, was added, with cooling to below +3° and vigorous stirring, to 200 ml of concentrated H_2SO_4. A mixture of 9.5 ml of concentrated HNO_3 (d, 1.5) and 50 ml of concentrated H_2SO_4 was then added slowly (vigorous mixing and cooling to below +3°). After 0.5 hour, the reaction mixture was poured onto ice (1 kg). Gradual neutralization with soda gave 38.5 g (quantitative yield) of 6-nitro-1-methylindoline, II; the substance was a bright red color, m. p. 49.5-50.5° (from aqueous methyl alcohol).

Found %: C 60.67; H 5.84; N 15.72. $C_9H_{10}O_2N_2$. Calculated %: C 60,66; H 5.65; N 15.73.

6-Nitro-1-methylindole, III. 15.7 g of II and 21.5 g of chloranil were dissolved in 300 ml of xylene and refluxed for 7 hours. After cooling, the solution was washed with 30% alkali, filtered, and again washed several times with alkali and then with water and dilute hydrochloric acid (1:3). The mixture was then washed with water, and the xylene was distilled under vacuum. Recrystallization from alcohol gave 14 g of III (90%), a bright yellow substance, m. p. 76.5-78.5° (from petroleum ether).

Found %: C 61.43; H 4.79; N 16.02. $C_9H_8O_2N_2$. Calculated %: C 61.35; H 4.57; N 15.90.

The substance did not form picrates.

6-Amino-1-methylindole, V. 15.7 g of III was dissolved in 150 ml of methyl alcohol, 5 g of Raney nickel was added, and 50 ml of hydrazine hydrate was added dropwise. Owing to exothermic heat, the temperature of the reaction mixture rose to 60°, and violent evolution of gas was observed. After an hour, the reaction mixture was carefully heated to 60°; it was then filtered, and the methyl alcohol was evaporated under vacuum. The V was distilled. The yield of V was 10 g (78%). B. p. 156° at 3 mm. It was a viscous liquid with a yellow color. It decomposed on standing.

Found %: C 73.69; H 7.26. $C_9H_{10}N_2$. Calculated %: C 73.93; H 6.89.

The hydrochloride of 6-amino-1-methylindole was prepared by passing a stream of dry hydrogen chloride into a solution of V in benzene. The salt gradually darkened on heating above 100°. It decomposed during an attempt to recrystallize it. It was hygroscopic in the presence of alcohol.

Found %: C 58.91; H 6.30. $C_9H_{11}N_2Cl$. Calculated %: C 59.17; H 6.07.

Schotten-Baumann benzoylation of V gave 6-benzoylamino-1-methylindole, X. The yield was quantitative. M. p. 159.5-160.5° (from alcohol, then from benzene, then from xylene).

Found %: N 11.01. $C_{16}H_{14}ON_2$. Calculated %: N 11.20.

The picrate of 6-benzoylamino-1-methylindole was an orange material. It was prepared in ether. M. p. 151-152° (from benzene).

Found %: N 14.55. $C_{22}H_{17}O_8N_5$. Calculated %: N 14.61.

6-Amino-1-methylindoline, VI. 17.9 g of II was dissolved in 100 ml of concentrated HCl, and 80 g of stannous chloride was added. An almost colorless salt of 6-nitro-1-methylindoline and stannic chloride precipitated. On heating on a boiling water bath, the crystalline double salt dissolved. After heating for 3 hours, the reaction mixture was cooled, and 40% alkali was carefully added to a strongly alkaline reaction. The reaction products were extracted with benzene, the benzene was distilled under vacuum, and the resulting material was distilled. 8.7 g of VI was obtained, b. p. 143-144° at 6 mm. M. p. 42-43°. It rapidly darkened in air.

Found %: C 73.09; H 8.38. $C_9H_{12}N_2$. Calculated %: C 72.93; H 8.16.

The benzoyl derivative, IX, was obtained in quantitative yield by Schotten-Baumann benzoylation. M. p. 149.3-149.6° (from ethyl alcohol).

Found %: C 76.09; H 6.49; N 11.13. $C_6H_{16}ON_2$. Calculated %: C 76.16; H 6.39; N 11.12.

The IX was dissolved in concentrated HCl, and the hydrochloride of 6-benzoylamino-1-methylindoline precipitated after a day. M. p. 255.5-256.5° (from alcohol).

Found %: C 66.41; H 6.27; N 9.65. $C_{16}H_{17}ON_2Cl$. Calculated %: C 66.54; H 5.94; N 9.70.

6-Phthalimino-1-methylindoline, VII. 5.5 g of 6-amino-1-methylindoline, VI, and 5.5 g of phthalic anhydride were heated on a bath at 200° for 30 minutes. Recrystallization from alcohol gave 10.2 g of VII (quantitative yield). M. p. 160-162°.

Found %: C 73.28; H 5.26; N 10.08. $C_{17}H_{14}O_2N_2$. Calculated %: C 73.36; H 5.07; N 10.06.

6-Phthalimino-1-methylindole, VIII. 2.78 g of VII was refluxed for 5 hours in 5 ml of xylene in a stream of carbon dioxide with 2.96 g of cinnamic acid and 0.1 g of palladium black. After cooling the reaction mixture, the solution was decanted from the palladium black, washed with 30% alkali, filtered and washed with alkali and then with water and with dilute acid (1:3). After washing with water, evaporation of the xylene solution under vacuum gave 1.7 g (63%) of 6-phthalimino-1-methylindole, VIII. M. p. 189-190° (from benzene and alcohol).

Found %: C 73.60; H 4.80. $C_{17}H_{12}O_2N_2$. Calculated %: C 73.89; H 4.38.

6-Amino-1-methylindole, V, from VIII. 1 g of VIII was dissolved in 15 ml of methyl alcohol, and heated to boiling with 1 g of hydrazine hydrate. After an hour, the alcoholic solution of V was filtered and poured into

water. It was extracted with ether, dried with $MgSO_4$, and distilled under vacuum. IV was obtained in the form of an oil. Benzoylation gave 0.6 g of 6-benzoylamino-1-methylindole, X, with a m. p. of 158-160°.

6-Nitro-1-methylisatin, IV. A solution of 5.2 g of CrO_3 in 15 ml of water was added dropwise and with stirring to a solution of 4.5 g of III in 180 ml of acetic acid. After 0.5 hour, 500 ml of water was added, and the IV was extracted with benzene (76% yield). The crystals were bright orange. M. p. 180-180.5° (from benzene).

Found %: C 52.54; H 3.11; N 13.62. $C_9H_6O_4N_2$. Calculated %: C 52.43; H 2.88; N 13.59.

The phenylhydrazone of IV was a dark red substance. M. p. 225-226° (from acetic acid).

Found %: C 60.78; H 4.39; N 18.90. $C_{15}H_{12}O_3N_4$. Calculated %: C 60.81; H 4.08; N 18.91.

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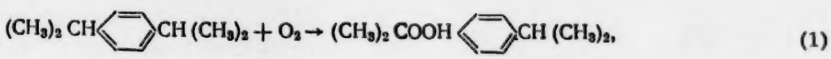
SYNTHESIS OF p-DIISOPROPYLBENZENE MONO- AND DIHYDROPEROXIDES

Academician A. V. Topchiev, I. F. Baev and L. A. Morozov

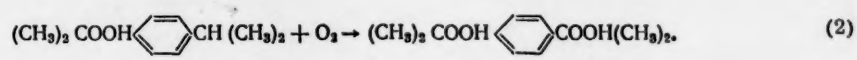
Industrial methods for the production of alkylbenzenes do not always yield alkylates suitable for liquid-phase oxidation. In this connection, the construction of high-tonnage industries has been determined by the technology of the production of isopropylbenzene from benzene and propylene in the presence of aluminum chloride catalyst. In the first place, this guaranteed successful utilization of the joint industrial production of phenol and acetone [1].

Mention has previously been made of the advisability of studying, along with the process of alkylation of benzene by olefins in the presence of boron trifluoride catalyst [2], the liquid-phase oxidation of alkylbenzenes obtained by this process [3]. In this communication are presented data on the liquid-phase oxidation of p-diisopropylbenzene produced by the above-indicated method.

In the course of the liquid-phase oxidation of p-diisopropylbenzene, the formation of mono- and dihydroperoxides proceeds according to the equations:



$$(CH_3)_2CH\text{-}C_6H_4\text{-}CH(CH_3)_2 + O_2 \rightarrow (CH_3)_2COOH\text{-}C_6H_4\text{-}CH(CH_3)_2, \quad (1)$$



$$(CH_3)_2COOH\text{-}C_6H_4\text{-}CH(CH_3)_2 + O_2 \rightarrow (CH_3)_2COOH\text{-}C_6H_4\text{-}COOH(CH_3)_2. \quad (2)$$

The p-diisopropylbenzene was separated from an alkylate produced in an apparatus having a capacity of 60-70 kg of isopropylbenzene and 7-10 kg/hour of p-diisopropylbenzene.

TABLE 1

Composition of Fractions Separated from Polyalkylbenzenes

Separation conditions and properties of fractions	Fraction		Kettle bottoms boiling at 234-236°
	I	II	
Top column temperature, °C	82-93	88-100	
Pressure during collection of fraction, mm Hg	28-40	13-31	atm.
Content of fraction, %	22.3	57	20
d_4^{20}	0.8542	0.8580	0.8628
n_D^{20}	1.48926	1.48976	1.4899

In an equilibrium experiment (No. 5), 2051 kg of a mixture having the following composition was obtained by the reaction of benzene with propylene in a ratio of 1 : 0.46 and with 0.00055 mole of catalyst per mole of benzene: unreacted benzene 38%, isopropylbenzene 50.4%, diisopropylbenzene and higher alkylbenzenes 10.6%.

Vacuum rectification of the polyalkylbenzene fraction in a column of 22-25 theoretical plates gave the fractions whose properties are presented in Table 1.

Pre-purified Fraction II, d_4^{20} 0.8585, n_D^{20} 1.48982, freezing point from − 20 to −23°, was used for the oxidation.

The properties of the diisopropylbenzene fraction did not agree with those cited by Melpolder [4] for pure p-diisopropylbenzene, d_4^{20} 0.85676, n_D^{20} 1.48983, f. p. −17.07°. Air with an oxygen content of 21-22% was used in the production of the hydroperoxides. The oxidation was carried out in a 3-liter, glass reactor fitted with a highly effective stirrer, a reflux condenser, a diffuser, an electric spiral heater, and the appropriate measuring and control apparatus.

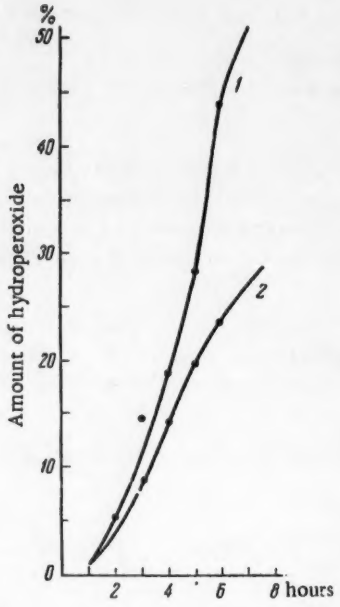


Fig. 1. Rate of formation of hydroperoxides in the reaction mixture as a function of time. 1) Calcalulated as monohydroperoxide; 2) calculated as p-diisopropylbenzene dihydroperoxide.

1.5 kg of diisopropylbenzene, 56 mg of divalent manganese, and 1.6 g of calcium hydroxide were used for the experiment. The reaction was carried out at a temperature of 112° ± 1°, and air feed rate of 65-70 liters/hour, and atmospheric pressure. Control of the formation of hydroperoxide in the reaction mixture was by iodometric titration and measurement of the refraction of samples collected from the reactor. The hydroperoxide concentration in the reaction mixture was not permitted to exceed 55% calculated as monohydroperoxide or 25% calculated as dihydroperoxide. The formation of hydroperoxide in the reaction mixture is shown as a function of time in Fig. 1.

Since the oxidation of p-diisopropylbenzene proceeds with the initial formation of monohydroperoxide and then dihydroperoxide, two curves are presented in the graph: Curve I, calculated as monohydroperoxide, and Curve II, calculated as dihydroperoxide.

At the conclusion of the oxidation, the resulting mixture was filtered at 100-105° from suspended material by means of a Schott filter. After this, the reaction mixture was separated into unreacted diisopropylbenzene, monohydroperoxide, and dihydroperoxide.

Characteristics of the diispropylbenzene oxidation and properties of the products obtained are presented in Table 2.

TABLE 2

Characteristics of the Oxidation of the Diisopropylbenzene Fraction

	Amount, g.	Content of major substance, %	d_4^{20}	n_D^{20}	M. p., °C
Taken for oxidation:					
p-Diisopropylbenzene	1500	–	0.8585	1.48982	−21
Air (liters)	700	21	–	–	–
Divalent manganese	0.056	6	–	–	–
Calcium hydroxide	1.5	98	–	–	–
Reaction mixture obtained	1532	56*	–	–	–
Including:					
p-Diisopropylbenzene	651	98	0.8584	1.48981	–
p-Diisopropylbenzene monohydroperoxide	637	91.4	0.9931	1.51280	–
p-Diisopropylbenzene dihydroperoxide	200	96.7	1.272	–	139
Diisopropylbenzene and other products from effluent gas	90	–	0.8587	1.4894	–

*Hydroperoxide calculated as monohydroperoxide.

The p-diisopropylbenzene monohydroperoxide isolated from the reaction mixture was an oily, colorless liquid with a content of the main material of 94.6%, boiling at a temperature of 98-112° and a residual pressure of 0.17-0.21 mm Hg, d_4^{20} 0.9932, n_D^{20} 1.51286. For a 14.1 % concentration of monohydroperoxide in p-diisopropylbenzene solution, the refractive index is n_D^{20}. The monohydroperoxide was mixed with refined p-diisopropylbenzene in a 2:8 weight ratio and again subjected to oxidation.

The resulting dihydroperoxide was purified by recrystallization from benzene. After purification, the dihydroperoxide was a white, crystalline solid with a content of dihydroperoxide of 99.8%, m. p. 140° ± 1° with decomposition, d_4^{20} 1.2724, n_D^{20} 1.38326 in 6% solution in isopropyl alcohol (pure isopropyl alcohol n_D^{20} 1.37664).

Thus, the p-diisopropylbenzene, obtainable as a by-product from isopropylbenzene production is a good starting material for the production of pi-diisopropylbenzene dihydroperoxide.

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A SPECIFIC, HIGHLY SENSITIVE FLUORESCENCE REACTION FOR ALUMINUM

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(Presented by Academician A. P. Vinogradov, August 3, 1957)

The most important organic reagents for aluminum are characterized by the presence of a hydroxyl group in the peri- or ortho-position to the atom forming the coordination bond. A large group of such reagents can be represented as follows [1, 2]:

Here, CB is the atom forming the coordination bond with the aluminum ion.

TABLE 1

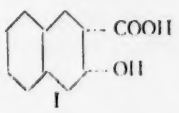
Comparison of the Most Sensitive Fluorescence Reactions for Aluminum

Reagent	Detectable minimum, γ	Dilution limit
Morin	0.005	$1:10^7$
1,4-Dihydroxy-5,8-dichloroanthraquinone	0.002	$1:10^6$
2-Hydroxy -3-naphthoic acid	0.0002	$1:10^7$

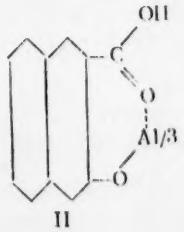
To this type of reagent belong many hydroxyanthraquinones, which react with aluminum ions with the formation of colored lakes or fluorescent reaction products. Thus, the highly sensitive fluorescence reaction with 1,4-dihydroxy-5,8-dichloroanthraquinone has been proposed for aluminum [3]; the reaction proceeds on heating and in the presence of calcium carbonate. The authors characterize this reaction as a specific reaction which can be carried out in a sufficiently acid medium; at high pH, one cannot consider the reaction specific, since, in this case, 1,4-dihydroxy-5,8-dichloroanthraquinone reacts with many other metal ions. The mechanism of this reaction has not been studied, and, in this connection, it may be mentioned that it is not known to which type of reaction it belongs – to the inner complex formation or to the adsorption type.

However, this reaction has been the most sensitive of all of the fluorescence reactions for aluminum known up to the present (Table 1).

Studying the analytical properties of certain aryl- and naphthyl carboxylic acids, we established that 2-hydroxy-3-naphthoic acid, I, is a highly sensitive, specific fluorescence reagent for aluminum.



I



II

In an aqueous solution with a pH above 2, 2-hydroxy-3-naphthoic acid has a green fluorescence under ultraviolet light; at a pH less than 2, it does not fluoresce; it fluoresces violet in benzene, lilac in chloroform, and green in alcohol; ether and carbon tetrachloride quench the fluorescence.

The vapors of 2-hydroxy-3-naphthoic acid fluoresce with a violet color, which makes it possible to assume the presence in aqueous solutions of dimers of this compound arising through hydrogen bonding; it is evident that the green color of the fluorescence must be ascribed to them.

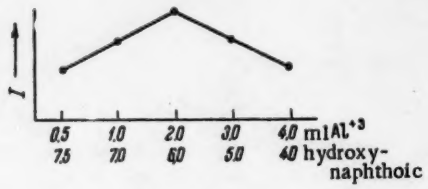


Fig. 1. Physiochemical analysis of the system Al^{3+} – hydroxynaphthoic acid (in solution). Along the abscissa are plotted the ratios of the volumes of the reacting components (molarity of the solutions of components was $1 \cdot 10^{-4}$).

A bright blue fluorescence observable under ultraviolet light arises from the reaction of 2-hydroxy-3-naphthoic acid with aluminum ions in aqueous solution at a pH of 3 and above.

This reaction was carried out as follows. A saturated aqueous solution of the reagent was added dropwise to 1 ml of the weakly acid solution being investigated; an excess of reagent should be avoided, since the green fluorescence of the reagent itself may mask the blue color from the reaction product. The sensitivity of the fluorescence reaction is 0.01 γ aluminum with a dilution limit of $1:10^6$.

The reaction can also be carried out by the spot method. Filter paper is saturated with the reagent solution and dried. Reagent solution is prepared as follows: about 0.1 g of 2-hydroxy-3-naphthoic acid and 0.2-0.3 g of urotropine are dissolved in 20 ml of water; if a residue of undissolved 2-hydroxy-3-naphthoic acid remained, it is filtered. The reagent paper fluoresces with a green color under ultraviolet light; moistening with water does not change the color of the fluorescence.

For the detection of aluminum, a drop of the solution being investigated is placed on the reagent paper and subjected to ultraviolet irradiation; the solution must be sufficiently acid (pH of 2-3). In the presence of aluminum, a blue fluorescence appears against the green background. The sensitivity of the drop method is 0.0002 γ aluminum with a dilution limit of $1:10^7$.

Ions of the following elements (in their ordinary valence state) do not interfere with the fluorescence drop reaction for aluminum with 2-hydroxy-3-naphthoic acid: Ca, Sr, Ba, Mg, Zn, Cd, Hg, Pb, Sn, Ti, V, As, Sb, Bi, Cr, Mo, W, Mn, Co, Ni, Cu.

In the presence of Th^{4+}, UO_2^{2+} and Fe^{3+} ions, a nonfluorescing field is generally formed in the center of the spot; this is explained by the fact that thorium ions exert a strong quenching effect, and UO_2^{2+} and Fe^{3+} ions form colored complexes with the reagent. However, owing to the considerable radial capillary movement of the aluminum ions (capillary separation), there is always formed a blue circle between the green background of the fluorescence reagent paper and the nonfluorescing dark spot. It should be noted that the sensitivity of the reaction decreases with a decrease in pH. At high pH (in the presence of free alkali), magnesium interferes with the detection of aluminum, the reagent being adsorbed on the surface of the $Mg(OH)_2$ and giving a similar fluorescence.

The proposal that the fluorescence reaction of aluminum with 2-hydroxy-3-naphthoic acid is adsorption has not been confirmed. In the first place, this is contradicted by the occurrence of a reaction at pH values lower than the values at which appreciable hydrolysis of aluminum salts begins. In the second place, the stoichiometric coefficients corresponding to which inner-complex formation proceeds have been determined by the method of physicochemical analysis [4, 5]. In Fig. 1, values of the intensity of fluorescence, I, are plotted along the ordinate.

From Fig. 1, it is seen that maximum fluorescence occurs when the ratio of the volumes of equimolar solutions of the components is equal to 1:3 (at a pH of 5).

On this basis, it can be assumed that the composition of the inner-complex compound formed corresponds to the formula $(C_{11}H_8O_3)_3Al$, which possibly has the structure II.

The colloidal state of the complex in the solution was established by Tyndall effect experiments.

The described fluorescence reaction can be used for the quantitative determination of traces of aluminum, and it is possible to work with concentrations from 0.1 γ to 0.01 γ per ml. It is recommended that the quantitative determination of aluminum be carried out by the use of a standard scale observable under ultraviolet light.

2-Hydroxy-3-naphthoic acid can be recommended as a fluorescent indicator with a range of 1.9-2.3 pH units.

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INVESTIGATION OF OXALATE AND CARBONATE COMPLEXES OF PLUTONIUM(IV) IN AQUEOUS SOLUTIONS BY THE SOLUBILITY METHOD

A. D. Gel'man and A. I. Moskvin

(Presented by Academician I. I. Cherniaev, August 15, 1957)

The data of Reas [1], who determined the solubility of Pu(IV) oxalate in oxalic acid of different concentrations (0.001-0.4 mole/liter) in the presence of 0.75 M HNO_3, are the only data in the published literature on oxalate complexes of Pu(IV). There is no information on the composition and stability of carbonate complexes of Pu(IV). There are only qualitative proofs of complex formation of Pu(IV) with carbonate ions [2a, b].

TABLE 1

Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in Mixed HNO_3–$(NH_4)_2C_2O_4$ Solutions ($\mu \cong 1$) in mole/liter

Concentration of $(NH_4)_2C_2O_4$	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$	Concentration of $(NH_4)_2C_2O_4$	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$
0.001	$6.19 \cdot 10^{-5}$	0.175	$2.38 \cdot 10^{-4}$
0.002	$5.02 \cdot 10^{-5}$	0.21	$3.35 \cdot 10^{-4}$
0.003	$4.58 \cdot 10^{-5}$	0.233	$4.18 \cdot 10^{-4}$
0.004	$4.06 \cdot 10^{-5}$	0.257	$5.36 \cdot 10^{-4}$
0.005	$3.55 \cdot 10^{-5}$	0.28	$6.87 \cdot 10^{-4}$
0.01	$4.3 \cdot 10^{-5}$	0.303	$8.92 \cdot 10^{-4}$
0.05	$5.77 \cdot 10^{-4}$	0.327	$1.135 \cdot 10^{-3}$
0.14	$1.8 \cdot 10^{-4}$	0.35	$1.37 \cdot 10^{-3}$

Results of the determination of the composition and instability constants of oxalate and carbonate complexes of Pu(IV) by the solubility method are presented below. First, the solubility of Pu(IV) oxalate in ammonium oxalate solutions of various concentrations (0.001-0.35 mole/liter) in the presence of 1.0 M HNO_3 was determined.

The experiments were carried out in a special apparatus for the determination of solubilities, in which were placed the solution and freshly precipitated Pu(IV) oxalate which had been first washed free of excess precipitant, $H_2C_2O_4$, with distilled water. The precipitate was stirred with a mechanical stirrer at 20 ± 0.02° for 4-6 hours. Preliminary experiments showed that this time was quite sufficient for the establishment of equilibrium in the system solution–solid phase. The concentration of plutonium in the equilibrium solutions was determined radiometrically.

The experimental data are presented in Table 1.

With an increase in the concentration of ammonium oxalate from 0.001 to 0.005 mole/liter, the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ decreased, achieving a minimum value of $3.55 \cdot 10^{-5}$ mole of Pu(IV) per liter, and then increasing owing to complex formation between pu(IV) and the oxalate ions. The solubility of Pu(IV) oxalate can be expressed by an equation of the form:

$$S = \frac{SP}{[C_2O_4^{2-}]^2}\left\{1 + \frac{[C_2O_4^{2-}]}{K_{n_1}} + \frac{[C_2O_4^{2-}]^2}{K_{n_2}} + \cdots \frac{[C_2O_4^{2-}]^m}{K_{n_m}}\right\}. \quad (1)$$

A calculation [3] with the aid of Equation (1) showed that in Pu(IV) oxalate solutions, the complex ions* $[Pu(C_2O_4)]^{2+}$, $[Pu(C_2O_4)_2]^0$, $[Pu(C_2O_4)_3]^{2-}$ and $[Pu(C_2O_4)_4]^{4-}$ are formed, the overall concentration instability constants of which are, respectively: $K_{n_1} = 1.8 \cdot 10^{-9}$, $K_{n_2} = 1.2 \cdot 10^{-17}$, $K_{n_3} = 4.0 \cdot 10^{-24}$ and $K_{n_4} = 3.3 \cdot 10^{-28}$. These instability constants correspond to complete decomposition of the Pu(IV) complex ions according to:

* Throughout the paper, by "composition of complex ions of Pu (IV)" is meant the ratio c. a. = central atom ligand in the inner sphere of the complex.

$$[Pu(C_2O_4)_{n_i}^{4-2n_i}] \rightleftarrows Pu^{4+} + n_i C_2O_4^{2-}. \quad (2)$$

The values of the over-all instability constants were used in the determination of the stepwise instability constants of oxalate complexes of Pu(IV) ions, which were successively: $K_1 = 1.8 \cdot 10^{-9}$, $K_2 = 6.7 \cdot 10^{-9}$, $K_3 = 3.3 \cdot 10^{-7}$ and $K_4 = 8.2 \cdot 10^{-5}$. These constants characterize the dissociation of the indicated Pu(IV) complex ions according to the equation:

$$[Pu(C_2O_4)_n^{4-2n_i}] \rightleftarrows \rightleftarrows [Pu(C_2O_4)_{n-1}^{6-2n_i}] + C_2O_4^{2-} \quad (3)$$

In accordance with this, the reactions of Pu(IV) complex formation, which proceed in solution, can be expressed by the following equations:

$$Pu^{4+} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)]^{2+}, \quad (4)$$

$$[Pu(C_2O_4)]^{2+} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_2]^0, \quad (5)$$

$$[Pu(C_2O_4)_2]^0 + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_3]^{2-}, \quad (6)$$

$$[Pu(C_2O_4)_3]^{2-} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_4]^{4-}. \quad (7)$$

In addition, the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ was determined in water and in the acids H_2SO_4, HNO_3, and $HClO_4$. The results of the experiments are presented in Table 2.

TABLE 2

Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in Water and Acids

Expt. No.	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in water, mg/liter	Concentration of H_2SO_4, N/liter	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, in water, mg/liter	Concentration of HNO_3, mole/liter	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, in water, mg/liter	Concentration of $HClO_4$, mole/liter	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in water, mg/liter
1	53	0.025	68	0.025	25	0.1	29
2	60	0.1	97	0.1	30	0.5	53
3	50	0.5	260	0.25	54	1.0	82
4	Ave 54	1.0	418	0.5	72	—	—
5	—	—	—	1.0	144	—	—

As seen from Table 2, the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in HNO_3 and $HClO_4$ is initially low in comparison with the solubility in water, and then, with an increase in the acid concentration to above approximately 0.1 N, it begins to increase. According to A. A. Grinberg and G. I. Petrzhak [4], the decrease in the solubility of $U(C_2O_4)_2 \cdot 6H_2O$ at low acid concentrations is due to the presence of acid properties in the substance per se. This explanation can also be applied to Pu(IV) oxalate. The acids may be arranged in the following series according to their tendency to interact with $Pu(C_2O_4)_2 \cdot 6H_2O$ in aqueous solution: $H_2SO_4 > HNO_3 > HClO_4$. The pH of the saturated aqueous solution of Pu(IV) oxalate was 4.4, and the molar electrical conductance was 470 Ω^{-1}.

The dissociation of Pu(IV) oxalate (by analogy with U^{4+}) can be represented by the following scheme:

$$[Pu(C_2O_4)_2(H_2O)_n] \overset{70\%}{\rightleftarrows} [Pu(C_2O_4)(H_2O)_{n-1}OH]^+ + H^+ + C_2O_4^{2-} \quad (8)$$

$$[Pu(C_2O_4)_2(H_2O)_n] \overset{30\%}{\rightleftarrows} [Pu(C_2O_4)(H_2O)_n]^{2+} + C_2O_4^{2-}. \quad (9)$$

On the basis of pH determinations and the electrical conductances of saturated and dilute aqueous solutions of $U(C_2O_4)_2 \cdot 6H_2O$, it has been proposed that, for U(IV) oxalate, the first process, acid dissociation, proceeds to the extent of 70%, and the second (salt dissociation) proceeds to the extent of 30% [4].

Using the indicated scheme, which approximately reflects the course of the processes in solution, the calculated electrical conductance is close to the experimental values for saturated and dilute aqueous solutions of

$U(C_2O_4)_2 \cdot 6H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$. Estimation of the acid dissociation constant of $Pu(C_2O_4)_2 \cdot 6H_2O$ gave a value of $\approx 3 \cdot 10^{-5}$.

TABLE 3

Solubility of Pu(IV) Hydroxide in Aqueous Solutions of K_2CO_3 at 20° (μ = const), mole/liter

Concentration of K_2CO_3	Solubility of Pu^{4+}	Concentration of K_2CO_3	Solubility of Pu^{4+}
0.362	$1.78 \cdot 10^{-4}$	2.896	$1.28 \cdot 10^{-3}$
0.724	$2.58 \cdot 10^{-4}$	3.261	$1.44 \cdot 10^{-3}$
1.448	$5.79 \cdot 10^{-4}$	3.62	$1.65 \cdot 10^{-3}$
2.172	$1.15 \cdot 10^{-3}$	—	—

The values of the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in mixed $HNO_3-(NH_4)_2C_2O_4$ solutions (see Table 1) were used for the determination, by graph, of the solubility product of Pu(IV) oxalate, which was equal to $4 \cdot 10^{-22}$. Approximately this same value was obtained for $SP_{Pu(C_2O_4)_2}$ by calculation using the data on the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in perchloric acid; the calculation was by means of the equation [5]

$$SP_{Pu(C_2O_4)_2} = [Pu^{4+}] [C_2O_4^{2-}]^2. \qquad (10)$$

We then carried out a determination of the solubility of Pu(IV) hydroxide in aqueous K_2CO_3 solutions of different concentrations and at constant ionic strength. The ionic strength of the solutions ($\mu \simeq 10$) was maintained constant by the addition of various amounts of KCl or $KClO_4$. The pH of the carbonate solutions was brought to 11.5 by means of KOH or HCl. The solution being investigated together with freshly precipitated hydroxide was stirred for 20-24 hours at a temperature of 20°. Preliminary experiments showed that the solubility of Pu(IV) hydroxide practically reached its equilibrium value in the indicated period of time. The results of the experiments are presented in Table 3.

For concentrations of K_2CO_3 of less than 1.45 mole/liter, the ionic strength was maintained at about 7.

The solubility of Pu(IV) hydroxide in a saturated solution of KCl ($\mu \simeq 3.5$) was $6.92 \cdot 10^{-6}$ mole/liter.

As seen from Table 3, the solubility of Pu(IV) hydroxide increased with an increase in the K_2CO_3 concentration owing to complex formation of Pu(IV) with carbonate ions. Calculations showed that, under these conditions, the complex ion $[Pu(CO_3)]^{2+}$ is formed with a concentration instability constant of $1.1 \cdot 10^{-47}$.

Along with these experiments, an investigation of the absorption spectra of the resulting solutions of Pu(IV) carbonate complex was carried out at room temperature in the region 400-1100 mμ using a SF-4 spectrophotometer. The absorption spectra of the Pu(IV) carbonate solutions had the most characteristic absorption maximums at wave lengths of 426, 472, 487, 640, 690-695, 764, 794, 848-850, and 1075 mμ.

By using data on the stability of oxalate complexes of the plutonium ion in its various valence states, it is possible to make a comparison of the relative tendencies toward complex formation of Pu(III), Pu(IV), and Pu(VI). As is well known, the dimension, charge, and structure of the cation, as well as other factors, have an effect on complex formation. The tendency toward complex formation increases with an increase in the polarizability of the ions, i.e., with an increase in the formal change and a decrease in the radius. In Table 4 are presented calculated values of the ionic potential [2c], $\varphi = z/r$ (where $\underline{z}$ is the ionic charge and $\underline{r}$ is the ionic radius in angstroms), which can be used for a comparison of the relative tendency toward complex formation of plutonium in its various stages of oxidation.

TABLE 4

Ionic Potentials of Plutonium in Various Valence States

Cation	r, Å	φ
Pu^{3+}	1.03	2.91
Pu^{4+}	0.90	4.44
PuO_2^+	0.87	1.15
PuO_2^{2+}	0.81	2.47

From these values, it is seen that the tendency toward complex formation of the various plutonium ions must decrease in the order $Pu^{4+} > Pu^{3+} \simeq PuO_2^{2+} > PuO_2^+$, i.e., in the order of decreasing ionic potential as presented in Table 4. The structure of the cation must have a strong effect on the stability of the complex ion. This is especially apparent with the plutonoyl and plutonyl ions. A comparison of the overall instability constants [5] of oxalate complex ions of Pu(III), Pu(IV), and Pu(VI) shows that the arrangement

TABLE 5

Dissociation Constants of Organic Acids and Instability Constants of Complex Ions of Pu(IV)

Acid	Dissociation constant of acid	Composition of Pu(IV) complex ion	Complex ion instability constant	Method of determination	Determined by
HCO_3^-	$4.6 \cdot 10^{-11}$	$[Pu(CO_3)]^{2+}$	$1.1 \cdot 10^{-27}$	Solubility	Gel'man and Moskvin
$HC_4H_4O_6^-$	$.5 \cdot 10^{-3}$	$[Pu(C_4H_4O_6)_3]^{2-}$	$5.0 \cdot 10^{-32}$	Polarographically	Vinogradov and Gryzin
$H_3C_6H_5O_7^-$	$1.74 \cdot 10^{-5}$	$[Pu(C_6H_5O_7)_2]^{2-}$	$6.0 \cdot 10^{-30}$	Same	Gel'man
$HC_2O_4^-$	$5.18 \cdot 10^{-5}$	$[Pu(C_2O_4)_4]^{4-}$	$3.3 \cdot 10^{-58}$	Solubility	and Moskvin
			$3.2 \cdot 10^{-58}$	Polarographically	Fomin et al

of Pu ions with respect to tendency toward complex formation as predicted from Table 4 is correct. The compositions of the complex ions are $[Pu^{IV}(C_2O_4)_2]^0$, $[Pu^{III}(C_2O_4)_2]^-$, and $[PuO_2^{VI}(C_2O_4)_2]^{2-}$. The overall instability constants are $1.2 \cdot 10^{-17} > 4.9 \cdot 10^{-10} \simeq 5 \cdot 10^{-13}$.

The tendency of Pu in its various valence states toward complex formation with anions of the types CO_3^{2-}, $C_6H_5O_7^{3-}$, $C_4H_4O_6^{2-}$, etc, will probably have the same order as in the case of the oxalates.

Another very interesting question is that of the effect on the tendency toward complex formation of dimensions, charge, and structure of anions of various acids. Using the data in Table 5, the anions can be arranged in the following series with respect to tendency toward complex formation with Pu(IV): $CO_3^{2-} > C_4H_4O_6^{2-} > C_6H_5O_7^{3-} \simeq C_2O_4^{2-}$.

A comparison of the over-all instability constants (see Table 5) with the dissociation constants of the organic acids confirms the point of view of Hindman [2d] on the correspondence between the strengths of hydrogen acids and the stabilities of complex ions formed by Pu(IV) with the anions of these acids.

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CONDENSATION OF ALKYLBENZENES WITH HALOGEN DERIVATIVES OF ISOBUTYLENE

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The alkylation of aromatic hydrocarbons with alkenyl halides using sulfuric acid as the catalyst is of undoubted interest, since it provides a simple method for the preparation of alkylaromatic compounds with a halogen atom in the alkyl radical. It has been established that allyl chloride [1], just as propylene, condenses with benzene in the presence of sulfuric acid, the reaction taking place at the double bond; β-chloroisopropyl benzene is the product. Later, methallyl chloride was used as the chloroalkylating agent, and boron trifluoride [2] and sulfuric acid [3] were used as catalysts. The yield of β-chloro-t-butylbenzene was 68% with a benzene: methallyl chloride: 96% sulfuric acid ratio of 3 : 1 : 0.15. Changing the ratio of reagents to 3.3 : 3.8 : 3.9, Schmerling and Ipatieff [4] obtained chiefly β-chloro-t-butylbenzene and bis(β-chloro-t-butyl)benzene with a yield of only 2.6%. On the chlorination of toluene with isocrotyl chloride [1-chloro-2-methylpropene], a product was obtained to which, without any proof, was ascribed the structure p-(β-chloro-t-butyl)toluene [5]. Having the problem of synthesizing alkylaromatic hydrocarbons and their derivatives containing side chains with a quaternary carbon atom attached solely to alkyl radicals, we carried out the condensation of methallyl chloride with alkylbenzenes:

$$C_6H_5R + CH = C(CH_3)CH_2Cl \xrightarrow{H_2SO_4} R - C_6H_4C(CH_3)_2CH_2Cl,$$

where R is CH_3-, C_2H_5-, iso-C_3H_7-, t-C_4H_9-, and $(CH_3)_3C-CH_2-$.

The conditions under which the condensations were carried out, the ratios of the reagents, the yields of products are presented in Table 1; the properties of the products are presented in Table 2. In all cases, the yield of condensation products was 64-98%, the actual yield depending on the order of addition of the reagents, as seen from Table 1 using t-butylbenzene as an example. When the acid was added to the mixture of t-butylbenzene and methallyl chloride (under the same conditions otherwise), the yield was 42%; when the methallyl chloride was added to the mixture of t-butylbenzene and sulfuric acid, the yield was 64%. The quantity of sulfuric acid and the temperature also had considerable effect. With a change in the ratio methallyl chloride: sulfuric acid from 1 : 0.15 to 1 : 0.5 and a decrease in temperature from 20 to 0°, the yield increased from 64% to 98%. We were able to isolated only p-(β-chloro-t-butyl)-t-butylbenzene from the products of the reaction of t-butylbenzene with methallyl chloride; this material is a solid which crystallizes readily from its mixture with the meta-isomer. The liquid residue and all other (β-chloro-t-butyl)alkylbenzenes, as was shown by infrared analysis were mixtures of the p- and m-isomers which could not be separated by fractional distillation nor by crystallization. Attempts were made to determine the ratio of isomers in the products of the condensation of methyl-, ethyl-, isopropyl-, and t-butylbenzene with methallyl chloride by oxidizing them with nitric acid and separating the resulting phthalic acids in the form of their barium salts [6]. However, in all cases we were able to isolate only terephthalic acid. On the basis of the oxidation data, which are presented under Experimental, it can be assumed that the m-isomer was formed in very small amounts, the major product being the p-isomer. In order to clarify the question of the relative reactivities of alkylbenzenes and benzene in the condensation reaction, an experiment was carried out in which an equimolar mixture of benzene and cumene was chloroalkylated with methallyl chloride. It was found that the reaction products contained approximately equal amounts of β-chloro-t-butylbenzene and β-chloro-t-butylcumene. With the aim of extending the number of haloalkylating agents, the condensation of benzene and t-butylbenzene with isocrotyl bromide [1-bromo-

2-methylpropene] was studied under the same conditions under which the condensation of these aromatic compounds with methallyl chloride was carried out. However, we were unable to obtain high yields of products in this case. It appeared especially interesting to carry out the condensation of benzene with 3-chloro-2-chloromethyl-1-propene. But in this case, 1,3-dichloro-2-methyl-2-phenylpropane was obtained in yields of only 3-6%. The major part of the 3-chloro-2-chloromethyl-1-propene underwent no change under the reaction conditions used. All of the β-chloro-(or bromo-) t-butylalkylbenzenes readily from organomagnesium compounds in good yields; these, in turn, can be used in Grignard reactions.

TABLE 1

Starting material	Ratio alkylben: halide: H_2SO_4	Reaction temp. °C	Concentration H_2SO_4, %	Reaction product	Yield, %
C_6H_6 и $H_2C{=}C(CH_3)CH_2Cl$	3 : 1 : 0.15	20	96	$C_6H_5{-}C(CH_3)_2CH_2Cl$ $p\text{-}ClCH_2C(CH_3)_2C_6H_4{-}{-}C(CH_3)_2CH_2Cl$ Contained m-isomer	64—66 2—4
Same	3 : 1 : 0.15	0—4	100	$C_6H_5C(CH_3)_2CH_2Cl$ $p\text{-}ClCH_2C(CH_3)_2{-}C_6H_4{-}{-}C(CH_3)_2CH_2Cl$ Contained m-isomer	72—74 4—6
" "	3 : 1 : 0.5	20	96	$C_6H_5{-}C(CH_3)_2CH_2Cl$ $p\text{-}ClCH_2C(CH_3)_2C_6H_4C(CH_3)_2{-}{-}CH_2Cl$ Contained m-isomer	60 12
C_6H_6 и $BrCH{=}C(CH_3)_2$	3 : 1 : 0.15	20	100	$C_6H_5{-}C(CH_3)_2CH_2Br$	23.5
Same	3,4 : 1 : 0.26	20	100	Same	35
C_6H_6 и $CH_2{=}C(CH_2Cl)_2$	3 : 1 : 1	20	96	—	—
Same	3 : 1 : 1	20	100	$C_6H_5C(CH_2Cl)_2{-}CH_3$	3.6
"	1.5 : 1 : 1	50—60	100	Same	3
" "	3.8 : 1 : 1	30	100	" "	6.3
$CH_3{-}C_6H_4$ и $H_2C{=}C(CH_3)CH_2Cl$	3 : 1 : 0.15	20	100	$p\text{-}CH_3{-}C_6H_4{\cdot}{\cdot}C(CH_3)_2CH_2Cl$ Contained m-isomer	74.5
$C_2H_5{-}C_6H_5$ и $H_2C{=}C(CH_3){-}CH_2Cl$	3 : 1 : 0.15	10	100	$p\text{-}C_2H_5{-}C_6H_4{-}C(CH_3)_2CH_2Cl$ Contained m-isomer	73
$i\text{-}C_3H_7{-}C_6H_5$ и $H_2C{=}C(CH_3){-}CH_2Cl$	3 : 1 : 0.15	10	100	$p\text{-}uC_3H_7{-}C_6H_4{-}C(CH_3)_2CH_2Cl$ Contained m-isomer	70
Same	3 : 1 : 0.3	10	100	Same	80
" "	3 : 1 : 0.5	0	100	" "	65.5
tert-$C_4H_9{-}C_6H_5$ and $H_2C{=}C(CH_3)CH_2Cl$	3 : 1 : 0.15	20	100	$p\text{-}tpet\text{-}C_4H_9{-}C_6H_4{-}C(CH_3)_2{-}{-}CH_2Cl$	
Same	3 : 1 : 0.15	20	100	Contained m-isomer	64
" "	3 : 1 : 0.3	10	100	Same	42
" "	3 : 1 : 0.6	10	100	" "	70.5
" "	3 : 1 : 0.5	0	100	" "	65.5
				" "	98—99
tert-$C_4H_9{-}C_6H_5$ and $BrCH{=}C(CH_3)_2$	1.5 : 1 : 0.15	20	100	$p\text{-}tert\text{-}C_4H_9{-}C_6H_4{-}{-}C(CH_3)_2CH_2Br$	23.5
$C_6H_{11}{-}C_6H_5{+}H_2C{=}C(CH_3){-}CH_2Cl$	3 : 1 : 0.5	30	96	$p\text{-}C_6H_{11}{-}C_6H_4{-}C(CH_3)_2CH_2Cl$	14
Same	3 : 1 : 0.5	20	96	Same	54

* The acid was added in 10-g portions over a period of an hour to the mixture of t-butylbenzene and methallyl chloride.

EXPERIMENTAL

Synthesis of the Original Halogen Derivatives of Isobutylene

Methallyl chloride was obtained by gas-phase chlorination of isobutylene. The product used in the condensation reactions had a b. p. of 70-71°/743 mm, n_D^{20} 1.4280. Literature data [7]: b. p. 71.5°/760 mm, n_D^{20} 1.4291.

Isocrotyl bromide was obtained in 47-50% yield by dehydrobromination of 1,2-dibromo-2-methylpropane. The dibromide, in turn, was obtained by the addition of bromine to isobutylene. 1.2 moles KOH in 180-200 ml

TABLE 2

Compound No.	Structural formula	B. p., °C/mm Hg	M.p., °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calc. from bond refr.,	Found C	Found H	Found Hal	Calculated C	Calculated H	Calculated Hal
1	$C_6H_5-C(CH_3)_2CH_2Br$	76.5/2	—	1.2818	1.5454	52.62	52.77	—	—	37.24 37.33			37.4
2	$C_6H_5-C(CH_2Cl)_2-CH_3$	76—77/1	—	1.1695	1.5498	55.06	54.71						
3	p-$CH_3-C_6H_4-C(CH_3)_2-CH_2Cl$												
	Contained m-isomer	82.5—84/1	—	1.0247	1.5240	54.55	54.61	72.28 72.31	8.06 8.16	18.92 19.07	72.31	8.27	19.40
4	p-$C_2H_5-C_6H_4-C(CH_3)_2-CH_2Cl$												
	Contained m-isomer	93—94/1	—	1.009	1.5210	59.36	59.30	73.51 73.45	8.76 8.62	17.87 18.07	73.26	8.71	18.02
5	p-u-$C_4H_9-C_6H_4-C(CH_3)_2CH_2Cl$												
	Contained m-isomer	110—112/3	—	0.9937	1.5156	64.18	63.98	74.33 74.47	9.16 9.14	16.66 16.52	74.09	9.09	16.83
6	p-tert-$C_4H_9-C_6H_4-C(CH_3)_2CH_2Cl$	113—114/1	53.5	—				74.95 74.99	9.24 9.43	15.89 15.46	74.80	9.41	15.77
7	Same							74.75	9.43	15.66			
	Contained m-isomer	107—108/1	—	0.9862	1.5140	68.12	68.66	74.65	9.25	15.99	74.80	9.41	15.77
8	tert-$C_4H_9-C_6H_4-C(CH_3)_2CH_2Br$	137—138/1	36.5	—	—	—	—	62.68 62.51	7.98 7.94	29.56 29.36	62.46	7.86	29.68
9	p-$C_5H_{11}-C_6H_4-C(CH_3)_2-CH_2Cl$							75.57	9.60	—			
	Contained m-isomer	114—116/1	—	0.9780	1.5145	73.57	73.35	75.38	9.59	—	75.43	9.79	—

of 75-95% ethyl alcohol was used for each mole of dibromide. In all, 900 g of isocrotyl bromide was obtained with a b. p. of 91-91.5° and n_D^{20} 1.4610. Literature data [8]: b. p. 91-91.3°, n_D^{20} 1.4603.

3-chloro-2-chloromethyl-1-propene was obtained in 60% yield by chlorination of methallyl chloride in the liquid phase. A total of 850 g of the dichloride was obtained with a b. p. of 133° and n_D^{20} 1.4750. Literature data [9]: b. p. 53°/45 mm, n_D^{20} 1.4740.

Synthesis of the Original Benzene Homologs

t-Butylbenzene was obtained by alkylation of benzene with t-butyl chloride in the presence of anhydrous ferric chloride [10]. B. p. 168-170°, n_D^{20} 1.4920. Yield 80%. Literature data [11]: b. p. 168.5-170°, n_D^{20} 1.4912.

Neopentylbenzene was obtained in 63% yield from t-butyl chloride and benzylmagnesium chloride. Distillation over sodium in a column gave a fraction boiling at 185-187°, n_D^{20} 1.4907. Literature data [12]: b. p. 185-186°, n_D^{20} 1.4885.

Condensation Reaction

The condensation reaction was carried out in a round-bottomed flask fitted with a stirrer, a dropping funnel, and a thermometer. The starting materials were usually calculated on the basis of 1 mole of isobutylene halogen derivative. Only in the condensation of neopentylbenzene with methallyl chloride and of benzene with 3-chloro-2-chloromethyl-1-propene were amounts of 0.5-0.8 mole used. The alkenyl halide was added, with vigorous stirring, to the mixture of alkylbenzene of sulfuric acid at a rate of 1 mole/hour. After completion of the addition, the reaction mixture was stirred for another 12 hours (longer stirring had no effect on the yield of reaction products). The contents of the flask were then washed twice with cold water and then with a weak solution of soda, and were dried over calcium chloride. The alkylbenzene and the original alkenyl halide were distilled at 40-80° and 90-100 mm Hg. The condensation products were separated by vacuum distillation.

Proof of structure of β-bromo-t-butyl bromide. A Grignard reagent was prepared from the bromide of the product of the condensation of benzene and isocrotyl bromide. Reaction of the Grignard with carbon dioxide gave β-phenylisovaleric acid, m. p. 58-59°.

Found %: C 74.32, 74.25; H 7.74, 7.86. $C_{11}H_{14}O_2$. Calculated %: C 74.12; H 7.92.

Literature data [3]: b. p. 58-59°.

Oxidation of the products of the condensations of alkylbenzenes with methallyl chloride. The oxidation was carried out with 20% HNO_3 in an autoclave at 200° for a period of 1.5 hours. 5-gram portions of the alkyl halides were used, and the 20% HNO_3 was taken in an amount 1.5 times greater than the calculated amount. The resulting phthalic acids were purified by conversion to their ammonium salts. The solutions were concentrated to small volumes by evaporation, and the ammonium salts were converted, in 66-70% yields, to the acids by acidification of the concentrated solutions. Refluxing of 1 g of the acids with 15 ml of methanol and 1.5 ml of concentrated H_2SO_4 gave, in all cases, 91-93% yields of dimethyl terephthalate with a m. p. of 141-142°; a mixture with a sample of known purity showed no melting point depression.

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THE EFFECT OF THE SIZE OF THE ALKYL RADICALS, R, ON THE STABILITY OF Si – R BONDS TOWARD THE ACTION OF CONCENTRATED SULFURIC ACID

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(Presented by Academician A. V. Topchiev, August 5, 1957)

In 1951, Sommer and co-workers [1] observed that the action of concentrated sulfuric acid on organosilicon compounds containing the $(CH_3)_3Si$ group leads to cleavage of a single methyl group, and, upon hydrolysis, a compound is formed which contains a siloxane bond. The intermediate product is an organosilicon sulfate [2] which is decomposed by the action of water with the formation of the $\equiv Si-O-Si \equiv$ bond. This reaction, new in the chemistry of organosilicon compounds, was carried out with a number of compounds containing various functional groups in the side chain (X): $-COOH$, $-NH_2$, and $-CO-CH_3$.

$$2\,(CH_3)_3\,Si\,(CH_2)_nX \xrightarrow[H_2O]{H_2SO_4} [X\,(CH_2)_n\,Si\,(CH_3)_2]_2\,O + 2CH_4.$$

Later, A. F. Plate, N. A. Belikova and Iu. P. Egorov [3, 4] established that a similar reaction takes place during the action of H_2SO_4 on silicohydrocarbons containing a five- or six-membered ring, the reaction occurring in the first case with only cleavage of the five-membered ring, and in the second case with cleavage of a methyl group along with cleavage of the six-membered ring. Compounds containing a four-membered ring behave similarly to the first case. The action of H_2SO_4 on dimethyltrimethylenesilane [1, 1-dimethyl-1-silacyclobutane] [5] leads only to ring cleavage. In contrast to these compounds, tetraethylsilane is very stable toward the action of concentrated H_2SO_4. Agitation of this compound with H_2SO_4 even for 9.5 hours causes cleavage of the $Si-C_2H_5$ bond only to the extent of 4-5 % [3].

The chemical stability of the $Si-C_2H_5$ bond was recently confirmed by us [6] for the case of the action of concentrated H_2SO_4 on methyldiethylsilylpropionic acid. It was found that only the $Si-CH_3$ bond undergoes cleavage.

From these data, it is possible to form the conclusion that the stability of the $\equiv Si-C \equiv$ bond with respect to the action of concentrated H_2SO_4 must depend on the size and structure of the hydrocarbon radicals joined to this carbon atom. In order to confirm this proposal, we have synthesized three new monobasic γ-organosilicon acids (VII, VIII, and IX) having the general formula $CH_3(R)_2SiCH_2CH_2COOH$ (where R is n-C_3H_7, n-C_4H_9, and i-C_5H_{11}), and we have studied their behavior toward the action of concentrated H_2SO_4 under standard conditions. As a result of these investigations, 3 new dibasic organosilicon acids were obtained: 4,4,6,6-tetra-n-propyl-4,6-disila-5-oxanonanedioic acid (X), 4,6-dimethyl-4,6-di-n-butyl-4,6-disila-5-oxanonanedioic acid (XI), and 4,6-dimethyl-4,6-diisoamyl-4,6-disila-5-oxanonanedioic acid (XII).

The structure of these acids indicates that rupture of the Si–C bonds in the original acids VII, VIII, and IX proceeded at different radicals. In acid VII, which contains the grouping $CH_3(n\text{-}C_3H_7)_2Si-$, cleavage occurred at the $\equiv Si-CH_3$ bond; the remaining two acids (VIII and IX), the $\equiv Si-C_4H_9$ and $\equiv Si-C_5H_{11}$ underwent cleavage:

$$CH_3(R)_2SiCH_2CH_2COOH \xrightarrow[H_2O]{H_2SO_4} \begin{cases} \xrightarrow{R = n\text{-}C_3H_7\ (X)} [HOOCCH_2CH_2SiR_2]_2O + 2CH_4 \\ \xrightarrow[R = n\text{-}C_4H_9\ (XI)\ \&\ i\text{-}C_5H_{11}\ (XII)]{} [HOOCCH_2CH_2Si(CH_3)R]_2O + 2RH \end{cases}$$

Our data confirmed the assumption that in γ-organosilicon acids containing the grouping $(CH_3)R_2Si-$; the order of cleavage of the $Si-CH_3$ and $Si-R$ bonds under the influence of concentrated H_2SO_4 is determined by the size of the hydrocarbon radical R. When R is C_2H_5 and n-C_3H_7, cleavage occurs at the $Si-CH_3$ bond; when R is n-C_4H_9 and i-C_5H_{11}, cleavage occurs at the C–R bond.

Thus, the radicals investigated for stability toward concentrated H_2SO_4 can be arranged in the following series:

$$C_2H_5, n\text{-}C_3H_7 > CH_3 > n\text{-}C_4H_9, i\text{-}C_5H_{11}.$$

The original monobasic organosilicon acids were prepared by the method described by Sommer and coworkers [7]. $CH_3SiCl_2(CH_2Cl)$ was prepared by photochemical chlorination of $(CH_3)_2SiCl_2$ [8], and converted to $CH_3(R)_2SiCH_2Cl$ by the action of RMgX.

The constants of the compounds prepared are presented in Table 1.

TABLE 1

Compound No.	Formula	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D calc.***	MR_D found
I*	$CH_3(n\text{-}C_3H_7)_2SiCH_2Cl$	191.5—192,5/758	1.4432	0.8882	53.64	53.37
II**	$CH_3(n\text{-}C_4H_9)_2SiCH_2Cl$	101.5—102/12	1.4475	0.8845	62.90	62.54
III	$CH_3(i\text{-}C_5H_{11})_2SiCH_2Cl$	124/10	1.4474	0.8731	72.16	71.93
IV	$CH_3(n\text{-}C_3H_7)_2SiCH_2CH(COOC_2H_5)_2$	155/7	1.4412	0.9520	84.75	83.93
V	$CH_3(n\text{-}C_4H_9)_2SiCH_2CH(COOC_2H_5)_2$	193/18	1.4445	0.9436	94.01	93.13
VI	$CH_3(i\text{-}C_5H_{11})_2SiCH_2CH(COOC_2H_5)_2$	174—175/5	1.4469	0.9317	103.27	102.81
VII	$CH_3(n\text{-}C_3H_7)_2SiCH_2CH_2COOH$	147.5/5	1.4508	0.9156	59.61	59.48
VIII	$CH_3(n\text{-}C_4H_9)_2SiCH_2CH_2COOH$	180.5/11	1.4510	0.9082	68.87	68.31
IX	$CH_3(i\text{-}C_5H_{11})_2SiCH_2CH_2COOH$	174.5/5	1.4536	0.8949	78.13	78.05
X	$[HOOCCH_2CH_2Si(n\text{-}C_4H_9)_2]_2O$	140—140,5/11	1.4560	0.9998	107.58	106.30
XI	$[HOOCCH_2CH_2Si(n\text{-}C_4H_9)(CH_3)]_2O$	154/8	1.4670	1.0125	98.32	99.35
XII	$[HOOCCH_2CH_2Si(i\text{-}C_5H_{11})(CH_3)]_2O$	155/17	1.4675	1.0064	107.58	106.90

* Literature data: b.p. 192°; n_D^{20} 1.4456 d_4^{20} 0.8902 [9].

** Literature data: b.p. 227.5°/767; n_D^{20} 1.4480; d_4^{20} 0.8827 [10].

*** MR_D calculated according to Warrik [11].

EXPERIMENTAL

Methyldi-n-propylchloromethylsilane (I). Prepared by the reaction of propylmagnesium bromide (prepared from 112 g (4.6 g-atoms) of magnesium and 738 g (6 moles) of n-propyl bromide) with 226 g (1.38 moles) of methyldichloro(chloromethyl)silane. Fractionation gave 105 g (0.58 mole) of I. Yield 42%.

Methyl-di-n-butylchloromethylsilane (II). Prepared by the reaction of butylmagnesium bromide (prepared from 150 g (6 g-atoms) of magnesium and 822 g (6 moles) of n-butyl bromide) with 410 g (2.5 moles) of methyldichloro(chloromethyl)silane. 270 g (1.3 moles) of II was obtained. Yield 52%.

Methyldiisoamylchloromethylsilane (III). Prepared by the reaction of isoamylmagnesium bromide (prepared from 109 g (4.5 g-atoms) of magnesium and 722 g (4.7 moles) of isoamyl bromide) with 256 g (1.6 moles) of methyldichloro(chloromethyl)silane. Fractionation gave 202 g (0.86 mole) of III. Yield 54%.

Found %: Si 11.54. $C_{12}H_{27}ClSi$. Calculated %: Si 11.95.

The methyldialkylsilylmethylmalonates, described below, were prepared by the reaction of sodiomalonic ester with methyldialkylchlorosilanes according to a method described in the literature [7].

Methyldi-n-propylsilylmethylmalonate (IV). Prepared by the reaction of sodiomalonic ester (prepared from 11.5 g (0.5 g-atom) of metallic Na, 800 ml of absolute ethanol, and 83.5 g (0.52 mole) of malonic ester with 90 g (0.5 mole) of I. Fractionation gave 96 g (0.31 mole) of IV. Yield 62%.

Found %: Si 9.36. E. No.* 374. $C_{15}H_{30}O_4Si$. Calculated %: Si 9.28. E. No. 370.

Methyldi-n-butylsilylmethylmalonate (V). Prepared by the reaction of sodiomalonic ester (prepared from 25.5 g (1.11 g-atom) of metallic Na, 800 ml of absolute ethanol, and 186.5 g (1.16 mole) of malonic ester) with 240 g (1.11 mole) of II. Fractionation gave 150 g (0.49 mole) of V. Yield 45%.

Found %: Si 8.48. E. No. 335. $C_{17}H_{34}O_4Si$. Calculated %: Si 8.50. E. No. 338.

Methyldiisoamylsilylmethylmalonate (VI). Prepared from 19 g (0.81 g-atom) of metallic Na, 800 ml of absolute ethanol, 132 g (0.82 mole) of malonic ester, and 190 g (0.81 mole) of III. Fractionation gave 160 g (0.45 mole) of VI. Yield 56%.

Found %: Si 7.86. E. No. 309. $C_{19}H_{38}O_4Si$. Calculated %: Si 7.83. E. No. 312.

These methyldialkylsilylmethylmalonates, IV, V, and VI, were converted to the monobasic acids by hydrolysis and decarboxylation with concentrated KOH (1:1) by a method described in the literature [7].

γ-Methyldi-n-propylsilylpropionic acid (VII). 90 g (0.3 mole) of IV was treated with concentrated alkali. 51.5 g (0.26 mole) of VII was obtained. Yield 85%.

Found %: Si 14.0. A. No.** 269. $C_{10}H_{22}O_2Si$. Calculated %: Si 13.87. A. No. 276.

γ-Methyldi-n-butylsilylpropionic acid (VIII). 145 g (0.44 mole) of V was treated with concentrated alkali. 93 g (0.4 mole) of VIII was obtained. Yield 91%.

Found %: Si 21.32. A. No. 239. $C_{12}H_{26}O_2Si$. Calculated %: Si 12.20. A. No. 243.

γ-Methyldiisoamylsilylpropionic acid (IX). 150 g (0.42 mole) of VI was treated with concentrated alkali. 85 g (0.33 mole) of IX was obtained. Yield 80%.

Found %: Si 10.84. A. No. 215. $C_{14}H_{30}O_2Si$. Calculated %: Si 10.86. A. No. 217.

The γ-methyldialkylsilylpropionic acids were reacted with concentrated sulfuric acid.

All experiments were carried out under the following standard conditions. Into a round-bottomed flask, fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer with a mercury seal, was placed concentrated H_2SO_4, sp. gr. 1.83, in an amount calculated on the basis of 200 ml per mole of organosilicon monobasic acid. The organosilicon acid was then added from the dropping funnel, with stirring, over a period of 1 hour. The reaction proceeded with the liberation of heat and the evolution of gaseous or low-boiling products. Stirring was continued for another 2 hours, after which the mixture was poured onto ice. The dicarboxylic acid, which separated in the form of a viscous oil, was extracted with ether, and the ethereal solution was washed with water, dried with anhydrous $CuSO_4$, the ether distilled, and the dicarboxylic acid was isolated by fractionation under vacuum.

Reaction of methyldi-n-propylsilylpropionic acid with H_2SO_4. 45 g (0.22 mole) of VII was added to 44 ml of H_2SO_4. Fractionation gave 32 g (0.08 mole) of 4,4,6,6-tetra-n-propyl-4-6-disila-5-oxanonanedioic acid (X). Yield 73%.

Found %: Si 14.40. A. No. 286. $C_{18}H_{38}O_5Si_2$. Calculated %: Si 14.37. A. No. 287.

* E. No. – ester number.

** A. No. – acid number.

Reaction of methyldi-n-butylsilylpropionic acid with H_2SO_4. 88 g (0.38 mole) of VII was added to 76 ml of H_2SO_4. Fractionation gave 62 g (0.17 mole) of 4,6-dimethyl-4,6-di-n-butyl-4,6-disila-5-oxanonanedioic acid (XI). Yield 90%.

Found %: Si 15.50. A. No. 299. $C_{16}H_{34}O_5Si_2$. Calculated %: Si 15.48. A. No. 309.

Reaction of methyldiisoamylsilylpropionic acid with H_2SO_4. 80 g (0.31 mole) of IX was added to 62 g of H_2SO_4. The reaction was accompanied by the evolution of a volatile product boiling at 27-29° (isopentane). Fractionation gave 47 g (0.12 mole) of 4,6-dimethyl-4,6-diisoamyl-4,6-disila-5-oxanonanedioic acid XII. Yield 77%.

Found %: Si 14.32. A. No. 287. $C_{18}H_{38}O_5Si_2$. Calculated %: Si 14.27. A. No. 287.

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TELOMERIZATION OF METHACRYLIC ACID WITH TRIALKYL PHOSPHITES

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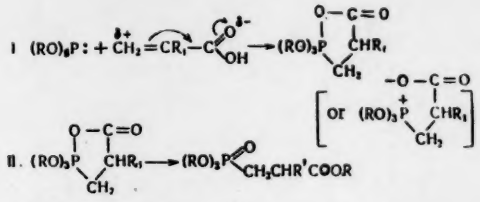
(Presented by Academician B. A. Arbuzov, November 13, 1957)

In previously published work [1], Gil'm Kamai and V. A. Kukhtin showed that trialkyl phosphites can undergo an Arbuzov rearrangement under the influence of α,β-unsaturated aldehydes and acids, the reaction proceeding, in the case of acids, according to the scheme:



Continuing the investigations in this field, we established that under well-known conditions, not one, but several molecules of methacrylic acid can be added to a molecule of triethyl phosphite, the reaction being of the nature of telomerization reaction in this case.

Carefully purified triethyl phosphite (purified with sodium and careful distillation) can be telomerized with methacrylic acid without a catalyst. The formation of telomer proceeds both at room temperature and on heating.

Phosphite purified by simple distillation does not telomerize with methacrylic acid.

However, in the case where the telomerization is carried out without a catalyst, the amount of telomer is very small. Therefore, it was first of all necessary to discover an appropriate catalyst for the telomerization of phosphites with methacrylic acid.

Connel and Coover [2], who recently described the telomerization of trialkyl phosphites with lactones, used triethylamine and sodium methylate as catalysts.

Experiments carried out by us showed that, although these two catalysts do bring about the telomerization of trialkyl phosphites with methacrylic acid, their use as catalysts is attended by difficulties, since it is difficult to obtain good reproducibility of the experiments; the yields of telomers are usually not large.

The most suitable catalyst for the telomerization of trialkyl phosphites with methacrylic acid is benzoyl peroxide. We studied the telomerization in the presence of various amounts of benzoyl peroxide and with various ratios of the starting components. In this manner, we obtained telomers with different average molecular weights.

All of the telomers obtained were white, powdery products which did not have definite melting points; on heating, they softened and carbonized; they were practically insoluble at room temperature in acetone, dioxane, benzene, nitrobenzene, carbon tetrachloride, ethyl alcohol, hexane, aniline, and chloroform. On heating, they dissolved in methanol and acetic acid.

The results of our experiments are presented in Table 1.

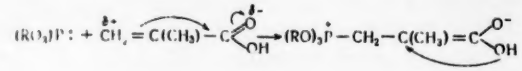
TABLE 1

Effect of Experimental Conditions on Average Molecular Weight and Degree of Polymerization (n) of the Telomers, $(RO)_2\overset{O}{\overset{\|}{P}}[CH_2CH(CH_3)COO]_nR$ (experiments carried out at 20°)

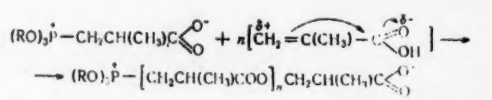
Expt. No.	Starting reagent	Mole ratio of reagents	Catalyst	Amount of catalyst, wt. %	Phosphorus content, %	n	Mol. wt. (Ave.) Calc.	Found (from phosphorus)	Deter. cryoscopically	Telomer yield, %
1	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 2	CH_3ONa	0.2	5.5	5	596	558	—	28.8
2	$(C_2H_5O)_2P$ $(CH_2=C-COOH)$ CH_3	1 : 2	$(C_2H_5)_3N$	0.4	5.4	5	596	582	—	25.2
3	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 1	$(C_6H_5COO)_2$	0.01	6.1	4	510	504	—	47.3
4	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 5	Same	0.01	3.9	7	768	752	665	44.4
5	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 10	. .	0.01	2.4	14	1371	1410	—	30.2
6	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 5	. .	0.001	5.9	4	510	515	—	14.3
7	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 5	. .	0.1	1.34	23	2144	2109	—	89.2
8	$(C_2H_5O)_2P^+$ $-O-C=O$ $CHCH_3$ CH_2 $CH_2=C-COOH$ CH_3	1 : 4	. .	0.01	4.6	6	682	680	—	51.2
9	$(C_2H_5O)_2P$ $CH_2=C-COOH$ CH_3	1 : 5	. .	0.2	3.4	8	896	930	856	34.5

Starting from our previously published work [1], it may be proposed that the telomerization proceeds according to the following scheme:

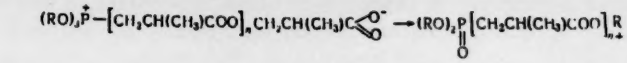
1. Chain initiation:



2. Chain growth:



3. Chain breaking



It is possible that the telomer has a different structure, provided chain growth proceeds by 1,2-addition, as occurs during the polymerization of acrylates, and not by 1,4-addition, as occurs during the interaction of α,β-unsaturated acids with phosphites. We did not study the structure of the telomer.

For confirmation of the proposed reaction scheme, we carrried out the following experiment. A mixture of equimolar amounts of triethyl phosphite and methacrylic acid was allowed to stand to the complete disappearance of the phosphite in the mixture. It was proposed that the intermediate product of the Arbuzov rearrangement was formed during this, corresponding to the first stage of the reaction. Then, a four-fold excess of methacrylic acid together with the benzoyl peroxide catalyst was added to the reaction mixture. Intensive formation of telomer began immediately. The telomer, obtained in good yield, was analogous in properties to that obtained in an experiment in which the components were at once combined in the same ratio (see Experiment Nos. 4 and 9).

First, this result confirms the formation of an intermediate product by the interaction of the trialkyl phosphite with the α,β-unsaturated acid, and, second, it confirms the liklihood of the proposed telomerization mechanism. The role of the catalyst, the mechanism of its effect on the telomerization, remains obscure.

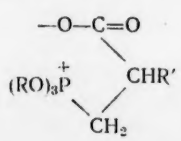
The experiments showed that the average molecular weight of the telomer increases with an increase in the concentration of methacrylic acid in the original mixture. Thus, under otherwise equivalent conditions, the average molecular weight of the telomer was 504 at a mole ratio of phosphite to methacrylic acid of 1:1, the molecular weight was 752 at a ratio of 1:5, and, at a ratio of 1:10, it became 1410 (see Table 1, Experiments Nos. 3, 4, and 5).

As shown by our experiments, with an increase in the concentration of benzoyl peroxide, the average molecular weight of the telomer increases (within the limits of the experiments). During telomerization of triethyl phosphite with methacrylic acid at a mole ratio of 1:5, the effect of benzoyl peroxide concentration on the average molecular weight of the telomer was as follows:

Concentration of benzoyl peroxide	Average molecular weight
0.1	2109
0.01%	752
0.001%	515

It is well known that the reverse relationship is usually observed during the polymerization of acrylates. Obviously, in the case of telomerization, an increase in the percentage of benzoyl peroxide leads to a weakening of the intensity of the telomerization, chain breaking proceeds more rapidly, and the reaction is steered chiefly in the direction of the Arbuzov rearrangement.

The ability of the intermediate product of the addition of tri-ethyl phosphite to methacrylic acid to enter into the telomerization reaction forces us to assume that the P—O bond in the ring has an ionic character. If the bipolar ion, formed initially in the course of the Arbuzov rearrangement, were stabilized in a cyclic intermediate product with a covalent P—O bond, it could hardly serve as a chain initiator during the telomerization; in any case, the telomerization would have proceeded less intensively than in the mixture of the starting components, while our experiments showed that during the interaction of methacrylic acid with the intermediate product, telomerization proceeded more intensively and was completed more rapidly than in the mixture of phosphite and acid. Therefore, the assumption follows that the intermediate product has the structure



It should be noted that Connel and Coover [2] also assumed the formation of an intermediate bipolar ion during the addition of phosphite to a lactone; furthermore, the reaction proceeded in two directions: in one, an Arbuzov rearrangement occurred leading to the formation of a phosphonocarboxylate, and in the other, under specific conditions, chain growth occurred with the formation of telomer.

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PREPARATION OF 2,3-DIMETHYLBUTADIENE BY A CATALYTIC ROUTE

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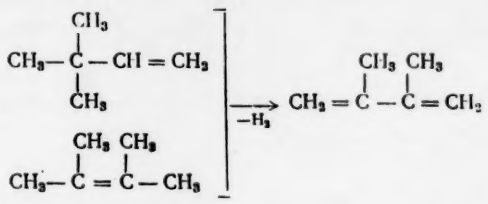
The aim of the present investigation was the synthesis of 2,3-dimethyl-1,3-butadiene, which is a possible starting material for the production of rubbery polymers as well as for a number of syntheses in preparative organic chemistry. The cheapest raw material for the synthesis of 2,3-dimethyl-1,3-butadiene is products of the hexane fraction from the processing of petroleum, which can be converted to branched hexanes and subsequently dehydrogenated in two stages. Of particular interest in the solution of the problem of using this raw material for the production of 2,3-dimethyl-1,3-butadiene is the second stage of the process, the dehydrogenation of the branched hexenes and, particularly of tert-butylethylene [3,3-dimethyl-1-butene] and of tetramethylethylene [2,3-dimethyl-2-butene] to 2,3-dimethyl-1,3-butadiene:



There are indications in the literature [1] that 2,3-dimethyl-1,3-butadiene can be obtained from 2,3-dimethylbutane by dehydrogenation of the latter over Al_2O_3 and Cr_2O_3, and there is also a patent [2] on the dehydrogenation of neohexane over Cr_2O_3/Al_2O_3 at 426-649° and a pressure of 4 atm. to a mixture of hexenes (yield 14-15%), of which 70% is trimethylethylene.

We dehydrogenated tert-butylethylene and tetramethylethylene over catalysts used for the commercial production of butadiene from butene. It was established that, under the conditions of the dehydrogenation, the first of these hydrocarbons is not converted to 2,3-dimethyl-1,3-butadiene, while dehydrogenation of tetramethylethylene does lead to the formation of 2,3-dimethyl-1,3-butadiene. The dehydrogenation was carried out at a temperature of 600-675°, space rates of 1000, 1500, and 2000 liters per liter of catalyst per hour, and a steam dilution of eight over K-12, K-18, and K-16 catalysts. The catalyzate was distilled, the fraction boiling at 68-75° was collected, and the diene content of this fraction was determined by condensation with maleic anhydride [3]; the 2,3-dimethyl-1,3-butadiene was separated from the 68-75° fraction by rectification. The effect of temperature and space rate on the course of the process was investigated with catalyst K-12. It was established that with an increase in temperature from 600 to 675°, the diene content of the condensate increases, the diene yield remains fairly constant, and the production of gas increases. Optimum conditions for the process are a temperature of 625-650° and a space rate of 1500 liters per liter of catalyst per hour. Under these conditions, the yield of diene remained fairly constant at 10-13% of the hydrocarbon fed and 25-30% of the hydrocarbon reacted. The results of the dehydrogenation over K-18 catalyst did not differ substantially from the results obtained with K-12 catalyst. Over K-16 catalyst, the yield of diene was 20-23% of the hydrocarbon fed and 40-50% of the hydrocarbon reacted.

* Deceased.

Work is currently continuing on the dehydrogenation of tetramethylethylene, unsymmetrical methylisopropylethylene, and 2,2- and 2,3-dimethylbutanes.

EXPERIMENTAL

tert-Butylethylene, b. p. 40°/760 mm, n_D^{20} 1.3760, d_4^{20} 0.6520, was prepared in 50% yield by pyrolysis of pinacolyl acetate [4]. Tetramethylene, b. p. 73°/760 mm, n_D^{20} 1.4122, d_4^{20} 0.7080, was prepared by dehydration of pinacolyl alcohol over $ZnCl_2$ on pumice at 192-200° [5].

The dehydrogenation was carried out in a quartz tube containing 5 ml of catalyst; the catalyst tube was contained in an electric tube furnace with an electronic temperature controller. The temperature was measured with a chromel-alumel thermocouple. The hydrocarbon and water were fed by means of a piston-type chemical proportioning pump. The gas was collected in a gasometer, and the liquid products and water were condensed in a cooled receiver. The hydrocarbon layer was separated and dried with $CaCl_2$. The hydrocarbon was distilled, and the fraction boiling at 68-75°, consisting of tetramethylethylene and diene, was collected. The 2,3-dimethyl-1,3-butadiene was identified as its addition product with maleic anhydride, 4,5-dimethyl-cis-Δ^4-tetrahydrophthalic anhydride, m. p. 74-76°(from petroleum ether with a 60-80 b.p.). The addition product was converted to 4,5-dimethyl-cis-Δ^4-tetrahydrophthalic acid, m. p. 187-192° (from aqueous alcohol) [6]. A check of the suitability of the maleic anhydride method [3] of determining dienes for use with a mixture of tetramethylethylene and 2,3-dimethyl-1,3-butadiene showed it to be completely applicable.

Dehydrogenation of tert-butylethylene over K-12 at 625°, a space rate of 1580 liters per liter of catalyst per hour, and a steam dilution of 7.7. 45.6 ml (0.353 mole) of hydrocarbon and 49.7 ml of water were fed. A hydrocarbon layer of 36 ml (21.7 g) and a water layer of 49 ml (2.7 moles) were collected. After an experiment, the system was purged with nitrogen to displace the residual gas. 10.25 liters (at standard conditions) of gas was collected. Distillation of the condensate: Fraction I – b. p. 28-40°, 2.5 g; Fraction II – b. p. 40-57°, 15.1 g; residue 0.8 g.

The results of the distillation show that the catalyzate did not contain a fraction boiling at 68-75°.

The course of the experiment is shown in Table 1.

TABLE 1

Time, minutes	Temperature °C	Hydrocarbon fed, ml	Water fed, ml	Gas collected, liters	Time, minutes	Temperature, °C	Hydrocarbon fed, ml	Water fed, ml	Gas collected, liters
Dehydrogenation of tert-butylethylene					Dehydrogenation of tetramethylethylene				
0	625	4.0	—	—	0	630	—	—	—
5	625	4.0	4.25	0.45	5	630	3.4	4.0	0.65
10	625	4.0	4.25	1.25	10	630	3.4	2.8	1.25
15	625	4.0	4.25	2.15	15	630	3.4	3.7	1.80
20	625	4.0	4.25	2.75	20	630	3.4	4.0	2.25
25	625	4.0	4.25	3.65	25	630	4.0	4.0	2.75
30	625	4.0	4.25	4.55	30	630	4.0	4.3	3.25
35	625	4.0	4.25	5.65	35	630	3.7	4.0	3.60
40	625	5.7	4.25	6.95	40	630	3.7	4.0	3.90
45	625	2.8	4.25	7.95	45	630	3.7	7.1	4.20
50	625	4.0	4.25	8.65	50	630	3.7	3.1	4.40
55	625	4.0	4.25	9.65	55	630	3.7	2.3	4.65
60	625	1.1	2.84	10.75	60	630	3.1	4.8	5.0

Dehydrogenation of tetramethylethylene over K-12 at 630°, a space rate of 1600 liters /hour, and a steam dilution of 7.3. The course of the experiment is shown in Table 1. 43.2 ml (0.363 mole) of hydrocarbon and 48 ml (2.6 moles) of water were fed. 36 ml (25 g) of hydrocarbon and 48 ml of water were collected. 6.4 liters (at standard conditions) of gas was collected. Composition of the gas (O_2- and N_2-free): CO_2, 5.4%; C_4 unsat, 9.73%; ethylene, 2.39%; H_2, 55.5%; saturates, 23%; CO, 4.04%. The weight of the gas was 1.26 g. The condensate was distilled, and the fraction (23.6 g) boiling at 68.74° was collected (2,3-dimethyl-1,3-butadiene content

TABLE 2

	600°	600°	612.5°	625°	625°	630°	627.5°	650°	675°
Yield of diene based on hydrocarbon fed, %	4.9	3.5	11.3	11.1	10.4	9.9	11.0	17.3	15.0
Diene based on CH_2On %	11.8	12.8	22.9	29.3	31.8	29.8	30.0	29.5	18.7
Diene catalyzate (frac. 68-74°), %	7.6	4.4	15.6	15.2	13.0	12.5	16.4	23.8	30.7

TABLE 3

	Space rate, 1/l/hr				
	1000	1000	1500	2000	
Diene (tetramethylene, %)	10.7	11.7	9.9	8.9	9.3
Diene (tetramethylene reacted, %)	22.6	20.6	29.8	20.1	24.8

TABLE 4

	Catalyst				
	K-12	K-18		K-16	
Diene (theoretical) tetramethylene fed, %	9.9	8.1	10.7	23.5	23.5
Diene (theoretical) tetramethylene reacted, %	29.8	31.0	31.8	49.6	50.8
Diene catalyzate (frac. 68-74°), %	12.5	9.6	13.6	30.4	30.0

TABLE 5

Fraction	B. p., °C	Residue	Diene content, %
I	34–55	13.6	—
II	61–68.3	4.8	54.6
III*	68.3–68.8	22.4	89.5
IV	68.8–70.2	8.6	64.1
V	70.2–71.6	15.0	26.8
VI	71.6–72	16.0	10.2
VII	72–72.8	122.6	—
Residue	—	7.0	

* Literature value [7], b.p. 2,3-dimethyl-1,3-butadiene 68.7°.

12.5%). 2.95 g of diene was collected. 9.9 g of tetramethylethylene reacted, and 20.7 g was recovered. The yield of diene was 9.9% of theoretical based on the hydrocarbon fed; the yield of diene based on reacted hydrocarbon was 30.5% of theoretical. The results of the experiments studying the effect of temperature are presented in Table 2.

The results of the experiments studying the effect of space rate at a temperature of 630° are presented in Table 3.

Data from experiments comparing K-12, K-18, and K-16 catalysts are presented in Table 4. The experiments were carried out at 630° and a space rate of 1500 liters/liter/hour.

III. Isolation of 2,3-dimethyl-1,3-butadiene. 210 ml of condensate (fraction boiling at 68-74°) was subjected to distillation in a column of 60 theoretical plates. The amounts and boiling points of the resulting fractions and their diene contents are presented in Table 5.

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INTRAMOLECULAR ACYLATION IN THE FERROCENE SERIES

CYCLIZATION OF γ-FERROCENYL-SUBSTITUTED AGIDS AND KETO ACIDS

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In a previous communication [1], using as an example the synthesis of di(ketotetrahydroindenyl)iron from di(ω-carboxyproply)ferrocene, we demonstrated the possibility of intramolecular acylation in the ferrocene series. The present work is an extension and continuation of the first communication. It was devoted to the cyclization of monosubstituted ferrocene derivatives.

By the interaction of β-carbomethoxypropionyl chloride with ferrocene, we obtained β-carbomethoxypropionylferrocene, and β-carboxypropionylferrocene was prepared from the latter.

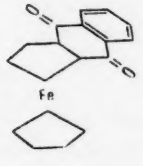
The attempted cyclization of β-carboxypropionylferrocene by the action of polyphosphoric acid or of sulfuric acid failed. Under mild conditions, the substance was recovered unchanged, and it decomposed under severe conditions.

The β-carboxypropionylferrocene was reduced by Clemmensen reduction to ω-carboxypropylferrocene. The latter, similarly to di(ω-carboxypropyl)ferrocene, cyclized readily on heating with polyphosphoric acid. This resulted in the formation of oxotetrahydroindenylcyclopentadienyliron. The structure of the latter was demonstrated: a) preparation of a derivative of the carbonyl group; b) by bromination, which led to pentabromocyclopentane, i.e., the presence in the molecule of an unsubstituted cyclopentadienyl ring was detected; c) by the infrared spectrum,* which confirmed the presence of an unsubstituted ring (frequencies: 1008 and 1106 cm^{-1}).

We also investigated the cyclization of o-carboxybenzoylferrocene. The o-carboxybenzoylferrocene was obtained by the interaction of ferrocene with o-carbomethoxybenzoyl chloride with subsequent hydrolysis of the resulting o-carbomethoxybenzoylferrocene.

In contrast to ferrocenyl-substituted keto acids of the aliphatic series, o-carboxybenzoylferrocene is readily cyclicized by both polyphosphoric acid and sulfuric acid. o-Carbomethoxybenzoylferrocene also cyclizes under these same conditions.

Thus, the analogy with benzene derivatives was complete. It is well known that benzoylpropionic acid does not cyclize, while o-benzoylbenzoic acid readily forms anthraquinone on simple heating [2].



Investigation of the structure of the cyclization product showed that it has structure I, since it forms pentabromocyclopentane on bromination, and its infrared spectrum contains lines characteristic of an unsubstituted cyclopentadienyl ring (frequencies: 1003 and 1107 cm^{-1}).

The results presented above confirm the conclusion, formed in the previous communication [1], that β-ferrocenyl-substituted carboxylic acids undergo intramolecular acylation in the same cyclopentadienyl ring to which the substituent is attached.

This even applies to o-carboxybenzoylferrocene in which this ring is somewhat deactivated by the presence of a CO group. β-Carboxypropionylferrocene does not cyclize.

* The spectra cited in the present paper were obtained by L. A. Kazitsyna and B. V. Lokshin.

Whether this is because the chain of four carbon atoms is not long enough to join the two cyclopentadienyl rings in ferrocene, or because the free ring is somewhat deactivated [3] by the first CO group is a question which will be resolved by future investigation.

EXPERIMENTAL

1. Preparation of β-carbomethoxypropionylferrocene. To a solution of 10 g (0.051 mole) of ferrocene in 100 ml of carbon bisulfide was added a solution of 7 g (0.05 mole) of $AlCl_3$ and 8 g (0.05 mole) of β-carbomethoxypropionic acid in 25 ml of absolute ether. After heating for an hour, the carbon bisulfide was decanted, and the residue was decomposed with ice and HCl. The resulting precipitate was twice recrystallized from a mixture of petroleum ether and benzene (3:1). This gave 5.2 g (32% of theoretical) of β-carbomethoxypropionylferrocene, an orange substance with a m. p. of 60°. The substance was readily soluble in alcohol, ether, benzene, and $CHCl_3$, and moderately soluble in heptane.

Found %: C 59.94, 60.15; H 5.13, 5.31; Fe 18.74, 18.56. $C_{15}H_{16}O_3Fe$. Calculated %: C 60.00; H 5.33; Fe 18.66.

The method is general for the preparation of monoacylferrocenes.

2. Preparation of β-carboxypropionylferrocene. 6.4 g of β-carbomethoxypropionylferrocene was heated for 5 hours with 30 ml of a 30% aqueous solution of KOH. The resulting alkaline solution was acidified, and 5.6 g (92.5% of theoretical) of β-carboxypropionylferrocene, a red-orange substance with a m. p. of 149-150° after recrystallization from 50% methyl alcohol, was obtained.

Found %: C 59.09, 58.93; H 4.97, 4.89; Fe 18.50, 18.48. $C_{14}H_{14}O_3Fe$. Calculated %: C 58.74; H 4.89; Fe 19.58.

3. Preparation of ω-carboxypropylferrocene. 1 g of β-carboxypropionylferrocene was reduced with a twenty-fold excess of amalgamated zinc and hydrochloric acid in glacial acetic acid (heated for 5 hours). This gave 0.89 g (97.8% of theoretical) of ω-carboxypropylferrocene with a m. p. of 117-118° after recrystallization from a mixture of petroleum ether and benzene (1:1).

Found %: C 61.85, 61.94; H 5.80, 5.93; Fe 20.22, 20.39. $C_{14}H_{16}O_2Fe$. Calculated %: C 61.76; H 5.88; Fe 20.58.

4. Cyclization of ω-carboxypropylferrocene. 2.1 g of ω-carboxypropylferrocene was mixed with polyphosphoric acid (prepared from 8 ml of H_3PO_4, sp. gr. 1.695, and 16 g of P_2O_5) and allowed to stand for 3 days at room temperature, and the mixture was then heated at 50-60° for 1 hour. The reaction mixture was then decomposed with alkali and ice, and the cyclization product was extracted with ether. This gave 1.05 g (56.4% of theoretical) of oxotetrahydroindenylcyclopentadienyliron, a yellow crystalline material with a m. p. of 84° after recrystallization from petroleum ether.

Found %: C 66.12, 66.01; H 5.61, 5.53; Fe 22.15, 22.08. $C_{14}H_{14}OFe$. Calculated %: C 66.14; H 5.51; Fe 22.04.

The semicarbazone of oxotetrahydroindenylcyclopentadienyliron, m. p. 198-198.5°, was prepared.

Found %: C 57.88, 57.83; H 5.64, 5.53; Fe 18.05, 17.95; N 13.6, 13.36. $C_{15}H_{17}ON_3Fe$. Calculated %: C 57.87; H 5.46; Fe 18.00; N 13.5.

5. Preparation of o-carbomethoxybenzoylferrocene. o-Carbomethoxybenzoylferrocene was prepared from 15 g (0.08 mole) of ferrocene in 150 ml of carbon bisulfide, 15.9 g (0.08 mole) of o-carbomethoxybenzoyl chloride, and 21 g (0.158 mole) of $AlCl_3$ in 60 ml of absolute ether under the same conditions used for β-carbomethoxypropionylferrocene. The yield of product was 23.2 g (82.8% of theoretical); m. p. 138° after recrystallization from 50% methyl alcohol and then from heptane (literature value: 134-135° [1]). A mixture with o-carbomethoxybenzoylferrocene prepared by esterification of o-carboxybenzoylferrocene [1] showed no melting point depression.

6. Preparation of o-carboxybenzoylferrocene. o-Carboxybenzoylferrocene was prepared, in 95% yield, by hydrolysis of o-carbomethoxybenzoylferrocene under the conditions described in Experiment 2. The red-orange substance decomposed at 183-184° after recrystallization from a mixture of water and CH_3OH (1:3) (see [1]).

Found %: C 65.10, 65.11; H 4.25, 4.16; Fe 15.92, 16.04. $C_{18}H_{14}O_3Fe$. Calculated %: C 64.68; H 4.22; Fe 16.71.

The potassium salt of o-carboxybenzoylferrocene, like the sodium salt [1], is difficultly soluble in water, and, during hydrolysis, it precipitates from solution as lustrous orange crystals.

7. Reduction of o-carboxybenzoylferrocene. 1 g of o-carboxybenzoylferrocene was reduced with a twenty-fold excess of amalgamated zinc and hydrochloric acid, the latter being added over a period of 10 hours while heating.

The product melted at 173-174° after recrystallization from a mixture of methyl alcohol and water (3:1). The yield of o-carboxybenzoylferrocene was 0.82 g (86% of theoretical).

Found %: C 67.41, 67.37; H 5.07, 5.14; Fe 17.62, 17.45. $C_{18}H_{16}O_2Fe$. Calculated %: C 67.5; H 5.00; Fe 17.45.

8. Cyclization of o-carbomethoxybenzoylferrocene. 3 g of o-carbomethoxybenzoylferrocene was mixed with 10 ml of concentrated sulfuric acid and allowed to stand for 10 hours, at room temperature. Then, with careful cooling, the reaction mixture was neutralized and the product extracted with ether. 1.45 g (54% of theoretical) of a yellow, crystalline material which did not melt above 300°, was obtained. This substance was soluble in benzene, alcohol, and toluene, and could be recrystallized from xylene.

Found %: C 68.36, 68.22; H 4.05, 4.02; Fe 17.19, 17.17. $C_{18}H_{12}O_2Fe$. Calculated %: C 68.38; H 3.83; Fe 17.66.

This same product was obtained in 34% yield by cyclization of o-carboxybenzoylferrocene under the conditions given above. Cyclization by means of polyphosphoric acid led to this same result.

9. Bromination of the products of the cyclization of ω-carboxypropylferrocene and of o-carboxybenzoylferrocene. Bromination of both products was carried out in the same manner.

The material being brominated was dissolved in CCl_4, a solution of bromine in CCl_4 was added, and the mixture was refluxed for 1-2 hours. After removal of the precipitated $FeBr_3$, the chloroform solution was evaporated, the oily part of the residue was washed with ether, and the precipitated crystalline pentabromocyclopentane was recrystallized from alcohol; m. p. 103-104° (literature value [4]: 103-104°). The sample was identified by mixed melting point with a known sample.

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** See C. B. Translation.

RHENIUM BORIDES

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(Presented by Academician I. I. Cherniaev, September 20, 1957)

If the sketchy reference by Heyne and Moers [1] to the preparation of rhenium-boron alloys by heating rhenium with BBr_3 is disregarded, there is practically no information in the literature on compounds of boron with rhenium. These compounds are of interest, first of all, because they should have characteristics resembling those of the stable, refractory, and solid tungsten borides [2] and other characteristics resembling those of the unstable manganese borides [3].

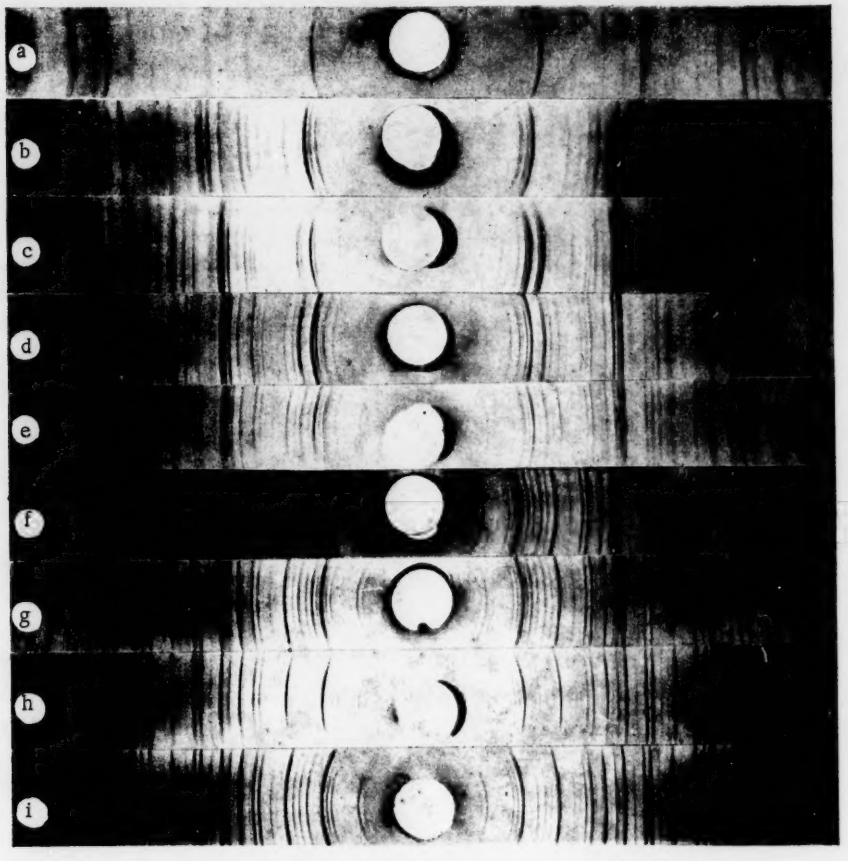

Fig. 1. X-ray patterns of alloys of the system Re–B. Boron contents in per cent: a) 0; b) 20; c) 33.3; d) 40; e) 50; f) 57.1; g) 60; h) 66.6; i) 71.3.

In this connection, the phase composition of rhenium-boron alloys was investigated in the present work, these alloys were prepared from relative amounts of rhenium and boron calculated on the basis of chemical compounds existing in systems of metals approximating rhenium in electronic structure and properties, i.e., in systems formed by tungsten, molybdenum, and manganese with boron: Re_4B, Re_2B, Re_3B_2, ReB, Re_3B_4, Re_2B_3, ReB_2, and Re_2B_5.

The alloys were prepared by sintering pressed mixtures of powdered rhenium and boron under vacuum at a temperature of 1900° for a period of 0.5 to 2 hours, using for this purpose a furnace lined with hot-formed boron carbide [4]. The original rhenium powder contained 99.966% Re and insignificant amounts of the following impurities: 0.008% K, 0.006% Na, 0.013% Ca, 0.003% Fe, 0.001% Al, 0.001% Cu, and 0.003% Ni. The boron powder was prepared by vacuum purification of magnesiothermic amorphous boron, and it contained 99.8% B.

The x-ray patterns were obtained by the powder method using copper radiation and an RKD camera of 57.3 mm diameter. The cylindrical samples, 0.8 mm in diameter, were prepared with a paraffin binder in order to prevent interaction with the atmosphere [5].

The x-ray patterns of the alloys are presented in Fig. 1. An attempt was made to identify the resulting alloys by comparing the positions of the lines on the powder patterns with the theoretically calculated positions of lines for analogous, known phases in other systems, the atomic radius of rhenium being taken as 1.373 A [6]. However, we were unable to obtain satisfactory correspondence of the structures of the rhenium-boron phases with the known boride phases.

Beginning with the composition Re_4B, there was a gradual change in the rhenium lattice. Along with the rhenium lines, which were considerably diffuse, there appeared a certain number of additional, weak lines, which were also diffuse. These lines became sharper with boron content up to 33 atom %. While attempting to interpret this γ -phase by means of Hull curves, it was found possible to fit the majority of the lines into a tetragonal system with the lattice constants: a = 5.47 and c = 4.73 A. A further increase in the boron content was also accompanied by gradual change in the powder patterns. Beginning at 50 atom % boron, the patterns of all samples were almost identical. In spite of the absence of significant changes on going from one alloy to the next, there was observed an appreciable change between the patterns of samples remote from one another with respect to composition. It should be noted that there is closer similarity among the patterns of alloys within the composition region 20-35 atom % B and among those of alloys within the composition region 40-80% B than there is among the patterns of alloys lying between these two regions. This provides a basis for assuming that there are two phases in the Re–B system, a γ -phase in the region 20-35 atom % B and a γ '-phase in the region of alloys containing more than 40 atom % boron; with an increase in boron content, the lattice of the γ '-phase also changes somewhat, and there is a transition to a phase with a somewhat changed structure. We were not able to identify this phase. Immediately after sintering, the alloy containing 33.3 atom % boron had a structure corresponding to the ϵ -phase of Me_2B_5 with the lattice constants a = 2.97 and c = 13.8 A; after long standing (for a month), it converted to the structure of the γ '-phase.

The thermal e. m. f. was measured for couples of the alloys with copper. In all cases, the sign of the thermal e. m. f. was negative. The thermal e. m. f. for alloys containing 30-40 atom % boron was 6-7μ v/degree, while for alloys containing 60-66 atom % boron it was 3-4μ v/degree. The change in the thermal e. m. f. could be connected with the transition from the γ - to the γ '-phase, which is apparently more ordered, and such an interpretation is in agreement with the x-ray patterns.

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THE ADDITION OF DIALKYL- AND DIPHENYLSILANES TO ETHYLENIC HYDROCARBONS

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The preparation of organosilicon compounds from unsaturated hydrocarbons was first described in 1947 [1, 2]. The authors showed that trichlorosilane and methyldichlorosilane add to unsaturated hydrocarbons in the presence of peroxide catalysts and under ultraviolet irradiation. In the succeeding years, a number of patents and papers described the interaction of various silicon compounds containing an Si−H bond with unsaturated hydrocarbons and other unsaturated compounds, and the effect of a number of catalysts on the reaction has been studied.

In 1954, Wagner [3] proposed the use of platinized carbon as a catalyst for the reaction of silicon compounds containing an Si−H bond with unsaturated compounds, and this catalyst proved to be more active than earlier catalysts.

In a series of previous communications [4-8], we reported studies on the addition of various silicon compounds containing an Si−H bond to unsaturated compounds.

The addition of diethylsilane, dibutylsilane, methylphenylsilane, and diphenylsilane to 1-octene, 1-nonene, and 1-decene was studied in the present investigation. The reactions were carried out in sealed tubes in the presence of platinized carbon.

The addition of diethylsilane and dibutylsilane to 1-octene and 1-nonene at a ratio of 1 : 2 proceeded at only one Si−H bond:

$$R_2SiH_2 + CH_2 = CH(CH_2)_5CH_3 \rightarrow R_2HSi - CH_2 - CH_2(CH_2)_5CH_3$$

where R = C_2H_5; C_4H_9.

Under the same conditions and at the same ratio of reactants, diphenylsilane added to 1-decene with the formation of diphenyldecylsilane, in 61% yield, and diphenyldidecylsilane, in 10% yield, according to the scheme:

$$C_6H_5|_2SiH_2 + CH_2 = CH(CH_2)_7CH_3 \rightarrow (C_6H_5)_2SiHC_{10}H_{21} + |C_6H_5|_2Si|C_{10}H_{21}|_2$$

Dibutylsilane did add to 1-nonene with the formation of dibutylnonylsilane (30.4% yield) and dibutyldinonylsilane (6% yield), but only at a ratio of 1 : 4.

Diphenylsilane also added to 1-decene in the presence of benzoyl peroxide, while diethylsilane did not add to 1-octene in the presence of benzoyl peroxide under the same conditions.

As seen from Table 1, diethylsilane and dibutylsilane added to olefins with yields which were half of those obtained with diphenylmethylsilane* and diphenylsilane.

On the basis of the experimental data obtained, it can be concluded that an Si−H bond in incompletely

* As in original – Publisher.

TABLE 1

Compound	Formula	B. p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% Yield
Diethyloctylsilane	$(C_2H_5)_2SiHC_8H_{17}$	105–107/5	0.7822	1.4377	67.14	67.58	20.5
Diethylnonylsilane	$(C_2H_5)_2SiHC_9H_{19}$	110–112/5	0.7894	1.4400	71.62	72.21	22.3
Dibutylnonylsilane	$(C_4H_9)_2SiHC_9H_{19}$	142–144/5	0.8008	1.4463	90.00	90.73	23.4
Phenylmethyloctylsilane	$C_6H_5CH_3SiHC_8H_{17}$	156–158/5	0.8658	1.4892	78.06	77.99	40.1
Phenylmethylnonylsilane	$C_6H_5CH_3SiHC_9H_{19}$	160–162/5	0.8663	1.4898	82.54	82.52	59.0
Diphenylnonylsilane	$(C_6H_5)_2SiHC_9H_{19}$	206–207/5	0.9419	1.5328	101.84	102.21	60.6
Diphenyldecylsilane	$(C_6H_5)_2SiHC_{10}H_{21}$	194–196/3	0.9441	1.5332	106.75	106.92	61.2
Dibutyldinonylsilane	$(C_4H_9)_2Si(C_9H_{19})_2$	215–218/5	0.8182	1.4548	131.49	132.14	56.8
Diphenyldinonylsilane	$(C_6H_5)_2Si(C_9H_{19})_2$	256–257/6	0.9154	1.5176	144.05	143.62	9.1
Diphenyldecylnonylsilane	$(C_6H_5)_2SiC_9H_{19}C_{10}H_{21}$	255–257/5	0.9189	1.5181	148.30	148.43	48.5
Diphenyldidecylsilane	$(C_6H_5)_2Si(C_{10}H_{21})_2$	261–266/5	0.9193	1.5187	153.38	152.88	10.0

substituted silanes containing phenyl radicals is more active in the addition to olefins than is an Si–H bond in incompletely substituted silanes with alkyl radicals.

Dibutyldinonylsilane and diphenylnonyldecylsilane were obtained from dibutylnonylsilane and diphenyldecylsilane, respectively, by reaction with 1-nonene.

EXPERIMENTAL

The dialkyl- and diphenylsilanes were obtained by replacement of chlorine by hydrogen in the corresponding dialkyl- and diphenylchlorosilanes by means of lithium hydride; their properties corresponded to the literature values.

Diethylsilane b. p. 54-56° at 754 mm; d_4^{20} 0.6834; n_D^{20} 1.3923.

Dibutylsilane b. p. 157-160° at 746 mm, d_4^{20} 0.7431; n_D^{20} 1.4219.

Phenylmethylsilane b. p. 140-143° at 751 mm; d_4^{20} n_D^{20} 1.5046.

Diphenylsilane b. p. 100-101° at 3 mm; d_4^{20} 0.9964; n_D^{20} 1.5756.

The experiments on the addition of dialkyl- and diphenylsilanes to olefins in the presence of platinized carbon were carried out in sealed tubes, which were held in a Carius-type furnace at a temperature of 160-180° for 10 hours.

Diethyloctylsilane. From 20 g (0.18 mole) of 1-octene and 8 g (0.09 mole) of diethylsilane, in the presence of 0.1 g of platinized carbon, was obtained 3.7 g (20.5% yield) of diethyloctylsilane; b. p. 107-109°/5 mm.

Found %: C 72.21, 72.19; H 14.11, 14.13. $C_{12}H_{28}Si$. Calculated %: C 72.00; H 14.00.

Diethylnonylsilane. From 15 g (0.12 mole) of 1-nonene and 5 g (0.06 mole) of diethylsilane, in the presence of 0.1 g of platinized carbon, was obtained 2.7 g (22.3%) yield of diethylnonylsilane, b. p. 110-112°/5 mm.

Found %: C 72.44, 72.44; H 14.14, 14.02. $C_{13}H_{30}Si$. Calculated %: C 72.34; H 14.10.

Dibutylnonylsilane and dibutyldinonylsilane.

a) 5.7 g (23.4% yield) of dibutylnonylsilane, b. p. 142-144°/5 mm, was obtained by reaction of 25 g (0.2 mole) of 1-nonene with 13 g (0.1 mole) of dibutylsilane in the presence of 0.2 g of platinized carbon.

Found %: C 75.55, 75.58; H 14.16, 14.15. $C_{17}H_{38}Si$. Calculated %: C 75.44; H 14.11.

b) 8.2 g (30.4% yield) of dibutylnonylsilane and 2.3 g (6% yield) of dibutyldinonylsilane were obtained by reaction of 52 g (0.41 mole) of 1-nonene with 14 g (0.1 mole) of dibutylsilane in the presence of 0.2 g of platinized carbon.

c) 3.7 g (56.8% yield) of dibutyldinonylsilane was obtained by reaction of 4 g (0.03 mole) of 1-nonene with 3.5 g (0.013 mole) of dibutylnonylsilane in the presence of 0.1 g of platinized carbon. The b. p. of the product was 215-218°/5 mm.

Found %: C 78.73, 78.71; H 14.09, 14.11. $C_{26}H_{56}Si$. Calculated %: C 78.78; H 14.14.

Phenylmethyloctylsilane. 6.1 g (40% yield) of phenylmethyloctylsilane was obtained by reaction of 15 g (0.13 mole) of 1-octene with 8 g (0.06 mole) of phenylmethylsilane in the presence of 0.15 g of platinized carbon. The b. p. of the product was 154-156°/5mm.

Found %: C 71.87, 71.91; H 13.98, 14.01. $C_{15}H_{26}Si$. Calculated %: C 72.00; H 14.00.

Phenylmethylnonylsilane. 5.9 g (59.1% yield) of phenylmethylnonylsilane was obtained by reaction of 10 g (0.08 mole) of 1-nonene with 5 g (0.04 mole) of phenylmethylsilane in the presence of 0.1 g of platinized carbon. The b.p. of the product was 160-162°/5 mm.

Found %: C 77.52, 77.50; H 11.32, 11.32. $C_{16}H_{28}Si$. Calculated %: C 77.73; H 10.92.

Diphenyldecylsilane and diphenyldidecylsilane.

a) 9.8 g (61.2% yield) of diphenyldecylsilane and 2.3 g (10% yield) of diphenyldidecylsilane were obtained by reaction of 14 g (0.1 mole) of 1-decene with 9 g (0.05 mole) of diphenylsilane in the presence of 0.1 g of platinized carbon.

b) The reaction was also carried out in a three-necked flask fitted with a stirrer. 28 g (0.2 mole) of 1-decene, 19 g (0.1 mole) of diphenylsilane, and 1 g of benzoyl peroxide were used in the reaction. The reaction mixture was heated for 16 hours at 80°. 13.2 g (41.2% yield) of diphenyldecylsilane was obtained.

The diphenyldecylsilane boiled at 194-196°/5 mm.

Found %: C 81.53, 81.35; H 9.74, 9.81. $C_{22}H_{32}Si$. Calculated %: C 81.48; H 9.87.

B. p. of the diphenyldidecylsilane was 259-260°/5 mm.

Found %: C 82.54, 82.61; H 10.87, 10.94. $C_{32}H_{52}Si$. Calculated %: C 82.76; H 11.20.

A diphenylnonylsilane and diphenyldinonylsilane. 7.5 g (60.6% yield) of diphenylnonylsilane and 1.6 g (9.1% yield) of diphenyldinonylsilane were obtained by reaction of 12 g (0.09 mole) of 1-nonene with 7.4 g (0.04 mole) of diphenylsilane in the presence of 0.1 g of platinized carbon.

The diphenylnonylsilane boiled at 206-207°/6 mm.

Found %: C 81.11, 81.07; H 9.42, 9.55. $C_{21}H_{30}Si$. Calculated %: C 81.29; H 9.67.

The diphenyldinonylsilane boiled at 256-260°/6 mm.

Found %: C 82.17, 82.17; H 11.01, 11.07. $C_{30}H_{48}Si$. Calculated %: C 82.56; H 11.01.

Diphenylnonyldecylsilane. 4.4 g (64.7% yield) of diphenylnonyldecylsilane was obtained by reaction of 4 g (0.03 mole) of 1-nonene with 5 g (0.015 mole) of diphenyldecylsilane in the presence of 0.1 g of platinized carbon. The product boiled at 225-257°/5 mm.

Found %: C 82.82, 83.00; H 10.92, 1.07. $C_{31}H_{50}Si$. Calculated %: C 82.66; H 11.11.

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VINYL COMPOUNDS IN THE DIENE SYNTHESIS

THE DIENE SYNTHESIS USING VINYL THIOETHERS WITH CYCLOPENTADIENE AND HEXACHLOROCYCLOPENTADIENE

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(Presented by Academician A. V. Topchiev, August 25, 1957)

It has previously been shown [1] that vinyl ethers of the formula $CH_2=CH-OR$, where R is alkyl, aryl, or a saturated hydroaromatic radical, can participate, as the dieneophile, in Diels-Alder reactions with cyclopentadiene and hexachlorocyclopentadiene:

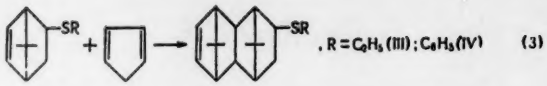
(1)

Prior known instances related to individual vinyl ethers, and the investigations were episodic in nature. Thus, Plate and Meerovich [2] prepared the addition product of cyclopentadiene and vinyl butyl ether. Abramov and co-workers [3] showed that it is possible to carry out Diels-Alder reactions between vinyl butyl and vinyl phenyl ethers and cyclones [cyclopentadienones].

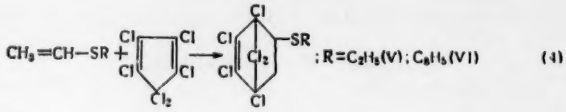
In a continuation of systematic study of Diels-Alder reactions involving vinyl compounds, we investigated the possibility of using thioethers. These compounds, individual representatives of which were prepared previously [4, 5], have become available owing to the development by one of us and Prilezhaeva [6] of a method for their preparation. The aim of the present work was to study reaction conditions for the Diels-Alder synthesis using vinyl ethyl sulfide and vinyl phenyl sulfide with cyclopentadiene and hexachlorocyclopentadiene.

There has been reported in the literature only one instance of the use of vinyl thioethers in Diels-Alder synthesis; in this case, p-tolylthiovinyl ether [p-tolyl vinyl sulfide] was used [7]. From the condensation of this compound with cyclopentadiene, Alder obtained a single adduct containing one molecule of the diene. We have previously noted [8] that vinyl aryl ethers display a greater tendency toward reacting by a radical mechanism than do vinyl alkyl ethers, and observations on the behavior of these and other compounds in the Diels-Alder synthesis disclosed that vinyl aryl ethers enter into this reaction more readily [1]. As regards vinyl sulfides, that they have a greater tendency toward free radical reactions in comparison with their oxygen analogs has also been noted [6]. On the basis of this similarity in the behavior of the indicated compounds, it would be expected that Diels-Alder reactions would proceed more readily with vinyl thioethers than with vinyl alkyl ethers, and this has been confirmed experimentally. Diels-Alder reaction of cyclopentadiene and hexachlorocyclopentadiene with vinyl thioethers proceeds at lower temperatures than with vinyl alkyl ethers, and, with the same reactant ratios, the yields of derivatives of vinyl thioethers is higher. The reaction resulted in the formation of thioethers of bicycloheptene and the corresponding derivatives of octahydronaphthalene.

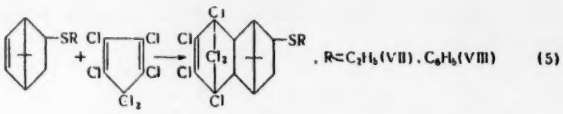
(2)



With hexachlorocyclopentadiene, vinyl thioethers form ethylmercapto- and phenylmercaptohexachlorobicycloheptenes:



The stepwise nature of the reaction is evident from the condensation of the resulting thioethers of bicycloheptene (I and II) with hexachlorocyclopentadiene to form thioethers of dihydroaldrin (VII and VIII).



Thus, conditions were found for the Diels-Alder reaction of vinyl ethyl and vinyl phenyl sulfides with cyclopentadiene and hexachlorocyclopentadiene. The resulting ethylmercapto- and phenylmercaptobicycloheptenes and hexachlorobicycloheptenes are derivatives of octahydronaphthalene and thioethers of dihydroaldrin. Thus, there is also a certain similarity in the behavior of vinyl aryl ethers and vinyl thioethers in Diels-Alder reactions with cyclopentadiene and hexachlorocyclopentadiene.

Reaction of vinyl ethyl sulfide with cyclopentadiene.* 6.6 g (0.05 mole) of dicyclopentadiene and 9.7 g (0.11 mole) of vinyl ethyl sulfide were heated in an autoclave (150 ml capacity) at 160° for 14 hours. After cooling of the reaction product and distillation of the excess vinyl ethyl sulfide, fractionation gave two products:

1) 2-Ethylmercaptobicyclo(2,2,1)-5-heptene (I), 4.5 g (42.7% of theoretical), b. p. 53.5-54°/2 mm, n_D^{20} 1.5160; d_4^{20} 0.9957; MR_D 46.81; $C_9H_{14}S$; calculated MR_D 46.87.

Found %: C 70.13, 70.00; H 9.11, 9.16; S 19.85, 20.06. $C_9H_{14}S$. Calculated %: C 69.88; H 9.19; S 20.75.

2) 1,4,5,8-Diendomethylene-2-ethylmercapto-(1,2,3,4,4a,5,8,8a)-octahydronaphthalene (III), 5.1 g (23.3% of theoretical). B. p. 122-123°/2 mm, n_D^{20} 1.5464; d_4^{20} 1.0652; MR_D 65.55; $C_{14}H_{20}S$; calculated MR_D 65.55.

Found %: C 76.17, 76.11; H 9.28, 9.32; S 14.34, 14.51. $C_{14}H_{20}S$. Calculated %: C 76.28; H 9.15; S 14.55.

Reaction of vinyl ethyl sulfide with hexachlorocyclopentadiene. A mixture of 2.25 g (0.025 mole) of vinyl ethyl sulfide and 6.75 g (0.025 mole) of hexachlorocyclopentadiene was heated in a flask, which was fitted with a reflux condenser, on a Wood's metal bath at 100-105° for 3.5 hours. Fractionation of the mixture gave 5.9 g (83% of theoretical based on the diene reacted) of 2-ethylmercapto-1,4,5,6,7,7a-hexachlorobicyclo-(2,2,1)-5-heptene (V) in the form of a viscous, light yellow liquid. B. p. 127-128°/2 mm, n_D^{20} 1.5668; d_4^{20} 1.5482; MR_D 76.15; $C_9H_8Cl_6S$; calculated MR_D 76.07.

*For convenience, dicyclopentadiene was used in the reaction; it decomposed under reaction conditions to the monomer. With monomeric cyclopentadiene, the reaction with vinyl thioethers can be carried out at a lower temperature.

Found %: C 30.37, 30.48; H 2.35, 2.29 S + Cl 68.34, 67.90. $C_9H_8Cl_6S$. Calculated %: C 29.94; H 2.23; S + Cl 67.80.

Reaction of 2-ethylmercaptobicyclo-5-heptene (I) with hexachlorocyclopentadiene. A mixture of 3.75 g (0.025 mole) of (I) and 6.75 g (0.025 mole) of hexachlorocyclopentadiene was heated at 120-130° for 4 hours, as described above. Fractionation of the mixture gave 1,4,5,8-diendomethylene-2-ethylmercapto-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VII) in an amount of 7 g (89.0% of theoretical based on the reacted (I)). B. p. 192-193°/2 mm.

Found %: C 39.57, 39.64; H 3.50, 3.57; S + Cl 56.50, 56.45. $C_{14}H_{14}Cl_6S$. Calculated %: C 39.34; H 3.31; S + Cl 57.33.

Reaction of vinyl phenyl sulfide with cyclopentadiene. 13 g (about 0.1 mole) of vinyl phenyl sulfide and 6.6 g (0.05 mole) of dicyclopentadiene were heated in an autoclave at 160-170° for 13 hours. Fractionation of the reaction mixture gave 8.5 g (42.0% of theoretical) of 2-phenylmercaptobicyclo(2,2,1)-5-heptene (II), a colorless material with a mild odor. B. p. 107-108°/1 mm, n_D^{20} 1.5925; d_4^{20} 1.0982; MR_D 62.38; $C_{13}H_{14}S$; calculated MR_D 61.74.

Found %: C 76.97, 77.03; H 7.11, 7.00; S 15.53, 15.89. $C_{13}H_{14}S$. Calculated %: C 77.20; H 6.98; S 15.82.

A pale yellow, tarry product, 1,4,5,8-diendomethylene-2-phenylmercapto-(1,2,3,4,4a,5,8,8a)-octahydronaphthalene (IV), was also isolated. B. p. 200-201°/4 mm. M. p. 67-68°.

Found %: C 80.18, 80.42; H 7.50, 7.76; S 11.84, 11.92. $C_{15}H_{20}S$. Calculated %: C 80.56; H 7.51; S 11.93.

The yield was 6.9 g (126.2 of theoretical).*

Reaction of vinyl phenyl sulfide with hexachlorocyclopentadiene. A mixture of 5.4 g (0.02 mole) of hexachlorocyclopentadiene and 2.8 g (0.02 mole) of vinyl phenyl sulfide was heated in a flask at 110-120° for 3 hours. Vacuum distillation of the product gave 0.5 g of unreacted diene and 5.9 g of yellow, oily, rapidly crystallizing 2-phenylmercapto-1,4,5,6,7,7a-hexachlorobicyclo(2,2,1)-5-heptene (VI). B. p. 190-191°/2 mm. M. p. 41-42°.

Found %: C 38.31, 38.22; H 1.95, 2.03; S + Cl 60.02, 60.42. $C_{18}H_8Cl_6S$. Calculated %: C 38.17; H 1.97; S + Cl 59.86.

The yield was 71.5% of theoretical.

Reaction of 2-phenylmercaptobicyclo(2,2,1)-5-heptene (II) with hexachlorocyclopentadiene. A mixture of 1 g (0.005 mole) of bicycloheptene (II) and 1.4 g (0.005 mole) of hexachlorocyclopentadiene was heated at 120-130° for 4 hours. 0.5 g of reactants was recovered in addition to 0.9 g of the addition product, a yellowish, vitreous mass. The 1,4,5,8-diendomethylene-2-phenylmercapto-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VII) had a b. p. of 257-258°/3 mm.

Found %: C 45.76, 45.97; H 2.69, 2.78. $C_{18}H_{14}Cl_6S$. Calculated %: C 45.64; H 2.96.

The yield was 36.0% of theoretical.

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THE ACTION OF CARBON DIOXIDE ON TRIALKYLALUMINUMS

SYNTHESIS OF CARBOXYLIC ACIDS

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(Presented by Academician A. N. Nesmeianov, September 19, 1957)

The information in the literature on the action of carbon dioxide on organoaluminum compounds is contradictory. Thus, Gilman and Marple [1] reported that p-toluic acid is obtained by the reaction of tri-p-tolylaluminum with carbon dioxide. Ziegler [2], in his recent review article, stated that the reaction of trialkylaluminums with carbon dioxide does not give carboxylic acids, and that the reaction of triethyl aluminum with carbon dioxide proceeds according to

$$3\,(C_2H_5)_3Al + CO_2 \rightarrow (C_2H_5)_3COAl(C_2H_5)_2 + (C_2H_5)_2AlOAl(C_2H_5)_2$$
$$\downarrow H_2O$$
$$(C_2H_5)_3C-OH$$

According to the data of Grignard and Jenkins [3], aliphatic organoaluminum compounds of the types R_2AlI and $RAlI_2$ do not, in general, react with carbon dioxide.

In the present work, we found that trialkylaluminums react with carbon dioxide under pressure and at an elevated temperature with the formation, chiefly, of carboxylic acids; under the conditions investigated, about two equivalents of the organoaluminum compound enter into the reaction. This at least indicates that it is a compound of the type $R_2AlOCOCH_3$ which reacts with the carbon dioxide to form the carboxylic acid. During the reaction of trialkylaluminums with carbon dioxide, along with the carboxylic acids we always obtained a certain amount of neutral substances, which were not investigated further in the present work.

The interaction of tripropylaluminum and carbon dioxide at a temperature of 220-240° gave butyric acid in a yield of 60% of theoretical:

$$(n\text{-}C_3H_7)_3Al + CO_2 \rightarrow (n\text{-}C_3H_7COO)_mAlR_{3-m} \rightarrow CH_3CH_2CH_2COOH.$$

Similarly, propionic and isovaleric acids were obtained from triethylaluminum and triisobutylaluminum, respectively. This method of synthesizing carboxylic acids from trialkylaluminums and carbon dioxide could be of considerable interest for the preparation of normal aliphatic acids of both the even and odd series; this method would start with triethyl- and tripropylaluminum and ethylene, and would proceed according to

$$(C_2H_5)_3Al + nC_2H_4 \rightarrow [H(CH_2CH_2)_{n+1}]_3Al \xrightarrow{CO_2} CH_3CH_2(CH_2CH_2)_nCOOH$$
$$(C_3H_7)_3Al + nC_2H_4 \rightarrow [CH_3(CH_2CH_2)_{n+1}]_3Al \xrightarrow{CO_2} CH_3(CH_2CH_2)_{n+1}COOH.$$

By the action of carbon dioxide on a mixture of trialkylaluminums, prepared directly from triethylaluminum and ethylene (see [2]), we obtained, with a yield of about 50%, a mixture of normal aliphatic acids of the uneven series, from which were isolated propionic, valeric, enanthic, pelargonic, and hendecanoic acids. In a

similar experiment with triproplyaluminum, a mixture of normal aliphatic acids was obtained, from which were isolated butyric, caproic, and caprylic acids.

EXPERIMENTAL

Reaction of tripropylaluminum with carbon dioxide. Synthesis of butyric acid. 29 g of tripropylaluminum in 200 ml of heptane and 40 ml of ether was charged to a pre-cooled (to −70°) 0.5-liter rocking autoclave and saturated with carbon dioxide from a cylinder. The autoclave was heated for 5 hours at 220-240°, the pressure increasing to 300 atm. After cooling the autoclave, the reaction mixture was removed, the solvent was distilled, and the precipitate was decomposed with 10% sulfuric acid. The sulfuric acid was extracted with ether. The ether extract was treated with a 10% solution of alkali. The alkaline solution was acidified, and the butyric acid was extracted with ether. 29.6 g of butyric acid was obtained; b. p. 114-115°/130 mm, n_D^{20} 1.3990. The anilide, m. p. 93-94° (from benzene), was prepared from the acid by the usual method; a mixture of the anilide with a known sample of butyranilide showed no melting point depression. 4.5 g of neutral material was also obtained.

Reaction of triethylaluminum with carbon dioxide. Synthesis of propionic acid. 30 g of triethylaluminum in 200 ml of heptane and 40 ml of ether was treated with carbon dioxide at 230-240°, as described in the preceding experiment. 24.1 g of propionic acid was obtained; b. p. 140-141°, n_D^{20} 1.3860. The anilide, m. p. 104° (from benzene), was prepared from the acid, and it gave no mixed melting point depression when tested with a known sample of propionanilide.

Reaction of triisobutylaluminum with carbon dioxide. Synthesis of isovaleric acid. 24.3 g of triisobutylaluminum in 200 ml of ether was charged to a pre-cooled (to −70°) autoclave and saturated with carbon dioxide from a cylinder. The autoclave was heated at 230-250° for 3.5 hours. The maximum pressure was 140 atm. After the usual treatment of the reaction mixture, 22 g of isovaleric acid was obtained; b. p. 95-96°/34 mm, n_D^{20} 1.4030. The anilide, m. p. 109° (from benzene), was prepared from the acid. Literature data [4]: isovaleranilide melts at 109-110°.

The action of carbon dioxide on a mixture of trialkylaluminums prepared from triethylaluminum and ethylene. 58.7 g of triethylaluminum in 100 ml of heptane was charged to an 0.5-liter autoclave and saturated with ethylene to a pressure of 40 atm. The reaction mixture was heated to 120-130°; the ethylene pressure fell almost to zero. After cooling the reaction mixture, it was diluted with 200 ml of heptane and 60 ml of ether, and transferred to a 1-liter autoclave, which had been pre-cooled to −70°. After saturation with carbon dioxide from a cylinder, the reaction mixture was heated at 200-220° for 3 hours. The usual treatment gave 85 g of a mixture of carboxylic acids and 25 g of neutral material. Vacuum fractionation of the product gave 10.1 g of propionic acid, b. p. 61-62°/30 mm, n_D^{20} 1.3860, 26.3 g of valeric acid, b. p. 105-107°/32 mm, n_D^{20} 1.4085, 18.3 g of enanthic acid, b. p. 133-135°/32 mm, n_D^{20} 1.4220, 10.2 g of pelargonic acid, b. p. 157-159°/30 mm, n_D^{20} 1.4321, 7 g of hendecanoic acid, b. p. 176-178°/30 mm (anilide, m. p. 70-71°), and 12 g of higher acids. Anilides were prepared from all of the acids, and their melting points agreed with the literature values.

The action of carbon dioxide on a mixture of trialkylaluminums prepared from tripropylaluminum and ethylene. 70 g of tripropylaluminum in 150 ml of heptane was charged to an 0.5-liter autoclave and saturated with ethylene to a pressure of 40 atm. The mixture was heated to 130-140°; the ethylene pressure dropped almost to zero. The reaction mixture was diluted with heptane to a total volume of 500 ml and transferred to a 1-liter autoclave, which had been cooled to −70°. After saturation of the reaction mixture with carbon dioxide from a cylinder, the autoclave was heated for 4 hours at 220-250°, the pressure rising to 320 atm. After the usual treatment of the product, 38 g of a mixture of carboxylic acids was obtained, from which were obtained by vacuum fractionation 8.1 g of butyric acid, b. p. 82-83°/30 mm, n_D^{20} 1.3992, 12.2 g of caproic acid, b. p. 119-120°/30 mm, n_D^{20} 1.4160, 6.8 g of caprylic acid, b. p. 146-148°/30 mm, n_D^{20} 1.4258 and 9 g of higher acids. Anilides were prepared from all of the acids; their melting points were in agreement with the literature values.

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CONDENSATION OF ACETALS WITH ETHOXYISOPRENE

A NEW METHOD OF SYNTHESIS OF POLYENIC ALDEHYDES OF THE ISOPRENOID TYPE

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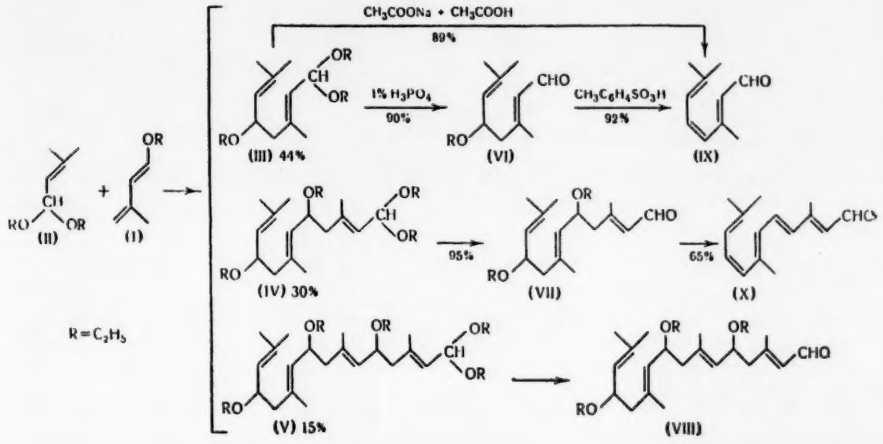
In recent years, vinyl ethers have been successfully used for the synthesis of polyenic aldehydes of the carotenoid series [1, 2].

Diene ethers have not previously been used for the preparation of aldehydes.

We decided to use ethoxyisoprene (3-methyl-1-ethoxy-1,3-butadiene), recently prepared in our laboratory [3], for the synthesis of polyenic aldehydes of the isoprenoid type. The use of ethoxyisoprene should permit the building up of the polyene chain by 5 carbon atoms at a time with the introduction of two double bonds and a methyl group in the positions required for isoprenoids.

We established that, under the influence of zinc chloride or boron trifluoride, acetals undergo 1,4-addition to ethoxyisoprene, I; this gives high yields of α,β-unsaturated ether acetals, which are then smoothly converted to ether aldehydes or polyenic aldehydes depending on the reaction conditions.

We studied this reaction in detail, using as the acetal that of dimethylacrylaldehyde, II. A mixture of ether acetals III, IV, and V was obtained in 89% yield by the reaction of acetal II with ethoxyisoprene, I, under the influence of zinc chloride at room temperature.



The formation of ether acetal IV is explained by the fact that ether acetal III, formed during the reaction, adds, in turn, to a second molecule of ethoxyisoprene. Ether acetal V is similarly formed from ether acetal IV and ethoxyisoprene.

* Deceased.

Isolation of ether acetal III in the pure form and its subsequent condensation with ethoxyisoprene, I, in the presence of zinc chloride gave ether acetals IV and V in yields of 41 and 25.5%, respectively.

The formation of high-molecular weight ether acetals is explained by the formation of an unsaturated ether acetal by the addition of an unsaturated acetal to ethoxyisoprene and the subsequent, rather easy reaction of the unsaturated ether acetal with a second molecule of ethoxyisoprene, etc. In order for the major products of the reaction to be ether acetals obtained by the addition of one and two molecules of ethoxyisoprene to the acetal, it is necessary to use an excess of the latter.

The ether acetals are entirely stable compounds, distillable under a vacuum of 0.1 mm without decomposition so that they may be separated without difficulty.

We found that the ether acetals are quantitatively hydrolyzed to ether aldehydes under the influence of 1% orthophosphoric acid.

4-Ethoxycitral, VI, 4,8-diethoxyfarnesal, VII, and 2,6,10,14-tetramethyl-4,8,12-triethoxy-2,6,10-14-hexadecatetraene-16-al, VIII, were prepared from ether acetals III, IV, and V.

The ether aldehydes were easily converted to polyenic aldehydes by the action of p-toluenesulfonic acid in toluene. Dehydrocitral (92% yield), IX, and farnesinal (65% yield), X, were obtained by this method from ether acetals VI and VII.

Dehydrocitral was also prepared in 89% yield directly from ether acetal III by heating the latter with a mixture of sodium acetate and acetic acid. An attempt to convert ether acetal to farnesinal X by this method was unsuccessful.

The use of ethoxyisoprene permits lengthening of the carbon chain by 5 carbon atoms with the introduction of two double bonds conjugated with an aldehyde group (in the case of the addition of one molecule of ethoxyisoprene) and by 10 carbon atoms with the introduction of four double bonds conjugated with an aldehyde group (in the case of the addition of two molecules of ethoxyisoprene); this is a new, simple method for the synthesis of polyenic aldehydes of the isoprenoid type.

EXPERIMENTAL

Condensation of dimethylacrylaldehyde acetal, II, with ethoxyisoprene, I. 35.6 g (0.32 mole) of ethoxyisoprene, I, was added over 2.5-hour period, with stirring, to a mixture of 204 g (1.3 mole) of acetal II and 13 ml of a 10% solution of zinc chloride in ethyl acetate at 20°; during the addition, the temperature rose to 27°. The reaction mixture was then stirred for 1.5 hours at room temperature and for 45 minutes at 35-40°, after which it was diluted with ether, washed with a 5% solution of sodium hydroxide and then with water, dried with potassium carbonate, and distilled under vacuum. There were obtained:

1) 159 g of the original acetal II, b. p. 65-68°/24 mm, n_D^{18} 1.4215.

2) 38.0 g (44% yield)* of 2,6-dimethyl-4,8,8-triethoxy-2,6-octadiene, III, in the form of a colorless liquid with a b. p. of 80-81°/0.1 mm, n_D^{20} 1.4517, d_4^{20} 0.9120; MR found 79.82, calculated 80.08.

Found %: C 71.28, 71.20; H 11.10, 11.11. $C_{16}H_{30}O_3$. Calculated %: C 71.08; H 11.19.

3) 18.0 g (30% yield) of 2,6,10-trimethyl-4,8,12,12-tetraethoxy-2,6,10-dodecatriene, IV, with a b. p. of 124-126°/0.04 mm, n_4^{20} 1.4618, d_4^{20} 0.9200; MR found 114.3; calculated 113.59.

Found %: C 72.24, 72.26; H 10.91, 10.91. $C_{23}H_{42}O_4$. Calculated %: C 72.18; H 11.06.

4) 7.8 g (15% yield) of 2,6,10,14-tetramethyl-4,8,12,16,16-pentaethoxy-2,6,10,14-hexadecatetraene, V, in the form of a yellowish, viscous liquid with a b. p. of 164-168°/0.07 mm, n_D^{20} 1.4710, d_4^{20} 0.9298.

Found %: C 73.00, 72.84; H 11.04, 10.84. $C_{30}H_{54}O_5$. Calculated %: C 72.85; H 11.00.

* Yield based on ethoxyisoprene.

Condensation of 2,6-dimethyl-4,8,8-triethoxy-2,6-octadiene, III, with ethoxyisoprene, I. By the method described above, from 12 g (0.044 mole) of ether acetal III, 2.5 g (0.022 mole) of ethoxyisoprene, and 0.6 ml of a 10% solution of zinc chloride in ethyl acetate were obtained 7.8 g of the original ether acetal III, 3.45 g of ether acetal IV, and 1.4 g of ether acetal V.

4-Ethoxycitral, VI. A mixture of 8.1 g of ether acetal III, 1 g of 1% orthophosphoric acid, and 2.5 ml of ethyl alcohol was stirred in a stream of nitrogen for 1.5 hours at room temperature. The reaction mixture became homogeneous after 15 minutes. The mixture was diluted with ether, washed with a 5% solution of sodium bicarbonate and then with water, dried with magnesium sulfate, and distilled under vacuum in a stream of nitrogen.

5.3 g of 4-ethoxycitral, VI, was obtained in the form of a colorless (yellowed on standing) liquid which did not have an odor of lemon peel; b. p. 58-60°/0.06 mm, n_D^{20} 1.4762, d_4^{20} 0.9247; MR found 59.89, calculated 58.34. λ_{max} (in ethanol) 240 mμ (log ε 4.132), 327 mμ (log ε 1.956).

Found %: C 73.29, 73.46; H 10.10, 9.98. $C_{12}H_{20}O_2$. Calculated %: C 73.41; H 10.27.

Dehydrocitral, IX. a) A mixture of 3.2 g of 4-ethoxycitral, VI, 50 ml of absolute toluene, and 5 mg of p-toluenesulfonic acid was heated on a Wood's metal bath at a bath temperature of 110-130°. The heating was accompanied by the distillation of toluene and alcohol; the distillation of alcohol ceased after 20 minutes (tested for alcohol content by the Chugaev-Tserevitinov method).

The reaction mixture was cooled, washed with a 5% solution of sodium bicarbonate and then with water, dried, and distilled under vacuum in a stream of nitrogen. 2.25 g of dehydrocitral, IX, b. p. 57-60°/0.05 mm, was obtained; it crystallized on cooling. After 2-fold recrystallization from petroleum ether, light yellow crystals of IX were obtained; m. p. 39-40°, which agrees with the literature value [4].

b) A mixture of 1) g of ether acetal III, 3.2 g of sodium acetate, 2 ml of water, and 30 ml of acetic acid was heated for 5 hours at 95° with stirring. After cooling, the reaction mixture was poured onto ice, and the oil which separated was extracted with petroleum ether. The extract was washed with a 5% solution of sodium bicarbonate and then with water, dried, and distilled under vacuum in a stream of nitrogen. 4.8 g of dehydrocitral IX, b. p. 64-65°/0.06 mm, was obtained. The m, p. of IX was 39-40 (from petroleum ether).

2,6,10-Trimethyl-4,8-diethoxy-2,6,10-dodecatriene-12-al (4,8-diethoxyfarnesal), VII. A mixture of 6.5 g of ether acetal IV, 0.75 g of 1% orthophosphoric acid, and 1.75 ml of ethyl alcohol was shaken in a sealed flask at room temperature. The stratification disappeared after 10 minutes; after standing for 1.5 hours, the mixture was subjected to the usual treatment, and was then distilled under vacuum in a stream of nitrogen. 5.02 g of 4,8-diethoxyfarnesal (VII) was obtained in the form of a yellow liquid with a b. p. of 114-115°/0.04 mm, n_D^{20} 1.4875, d_4^{20} 0.9419; MR found 94.28, calculated 91.84.

Found %: C 73.99, 74.13; H 10.43, 10.44. $C_{19}H_{32}O_3$. Calculated %: C 73.98; H 10.46.

Farnesinal, X. A mixture of 2 g of undistilled 4,8-diethoxyfarnesal, VII, 50 ml of absolute toluene, and 6 mg of p-toluenesulfonic acid was heated in an atmosphere of nitrogen on a Wood's metal bath at a bath temperature of 120-125°. Slow distillation of toluene and alcohol occurred, and toluene was simultaneously added to the flask at a rate such that the volume of the reaction mixture remained constant. Distillation of alcohol ceased after an hour (distillate tested for alcohol content by the Chugaev-Tserevitinov method). After the usual treatment of the reaction mixture and its distillation under vacuum in a stream of nitrogen, there was obtained 0.85 g of a material with a b. p. of 115-120°/0.05 mm, which began to crystallize during the distillation. After 2-fold recrystallization from ethyl alcohol, farnesinal, X, was isolated in the form of yellow petals with a m. p. 119-120, which agrees with the literature value [4].

λ_{max} (in ethanol) 239 mμ (log ε 3.92).

Found %: C 83.40; H 9.41. $C_{15}H_{20}O$. Calculated %: C 83.23; H 9.32.

2,6,10,14-tetramethyl-4,8,12-triethoxy-2,6,10,14-hexadecatetraene-16-al, VIII. A mixture of 3 g of ether acetal V, 0.75 g of 1% orthophosphoric acid, and 1.75 ml of ethyl alcohol was shaken in a sealed flask at room temperature.

The mixture was shaken for 1.5 hours, and was then subjected to the usual treatment. 1.9 g of ether acetal VIII was obtained in the form of a thick, yellow liquid with a b. p. of 158-162°/0.1 mm, n_D^{20} 1.4954, d_4^{20} 0.9452.

Found %: C 74.06, 74.30; H 10.24, 10.20. $C_{25}H_{54}O_6$. Calculated %: C 74.27; H 10.54.

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THE RECRYSTALLIZATION DIAGRAM OF TANTALUM

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(Presented by Academician I. P. Bardin, August 3, 1957)

The high corrosion resistance of tantalum in corrosive media, its refractoriness, its high plasticity, which permits plastic deformation in the cold at a high degree of reduction while retaining adequate strength, and a number of other properties have promoted the use of tantalum as one of a number of technically important metals. As is well known, grain size is a very essential factor affecting the mechanical properties of metals and alloys, and, therefore, construction of the structural diagram, which relates grain size to degree of deformation and temperature of the subsequent annealing, is particularly necessary for metals used chiefly in the form of products made by means of deformation (sheets, foil, bar stock, pipe, wire, etc.). Such data permit selection of conditions for deformation and annealing which guarantee optimum mechanical properties of the product. The recrystallization diagram of tantalum has not yet been published. The literature contains only some data on the recrystallization of cold-worked tantalum, the data relating to tantalum produced by the metal-ceramic method [1-3]. There are no data in the literature on the recrystallization of tantalum produced by casting.

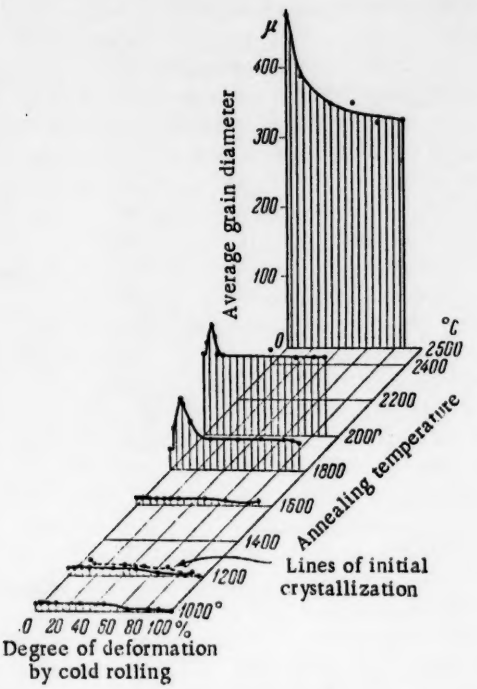

Fig. 1. Recrystallization diagram of tantalum.

Up to the present, the chief method for the production of massive tantalum, as well as of other refractory metals (tungsten, niobium, molybdenum), is powder metallurgy. Recently, arc melting has received widespread development; the process is carried out under vacuum or in the presence of an inert atmosphere, and is useful for such refractory and easily oxidized metals as titanium, zirconium, molybdenum, etc. Arc melting of molybdenum and, particularly, of its alloys has replaced production of metal-ceramic castings. Therefore, the study of the recrystallization of cast tantalum is of great interest. We constructed the Type I recrystallization diagram of tantalum for cold deformation obtained by rolling cast tantalum (Fig. 1). Casting of the samples was carried out in an arc furnace in argon at a pressure of 200 mm Hg; the starting material was metal-ceramic tantalum foil of 99.8% purity.

Cooling of the metal in a copper hearth promoted the formation of a coarsely crystalline structure (Fig. 2a).

Cast bars were cold-forged until a cross section of 7 × 7 mm was obtained, and the resulting rods were then annealed in a vacuum at 1300° for 2 hours. As a result of this treatment, the coarsely crystalline structure of the cast metal was completely eliminated. The rods possessed a recrystallized, fine-grained,

polyhedral structure with a grain diameter of 10-11 μ (Fig. 2b), and they served as the starting material for all of the work.

Deformation of these rods was carried out by cold rolling without intermediate annealing; 13 degrees of reduction were used: 2.6, 5.7, 8, 10, 15, 34, 50, 68, 83, 90, 96, and 98.6%. The deformed rods were cut into samples 8-10 mm long, and were annealed under vacuum in the temerature interval 1000-2500° with a soaking time of 1 hour. Determination of the grain size was carried out by means of an objective micrometer; the measurements were made on a cross section of a thin section at the site of the intersection of the diagonals, which corresponds to the zone of maximum deformation. The temperature of the beginning of recrystallization was determined by the microstructural method and by the x-ray method by the appearance of the first spots on the diffraction rings. The x-ray exposures were made with Cu radiation using a section which had first been deeply etched to remove the surface layer.

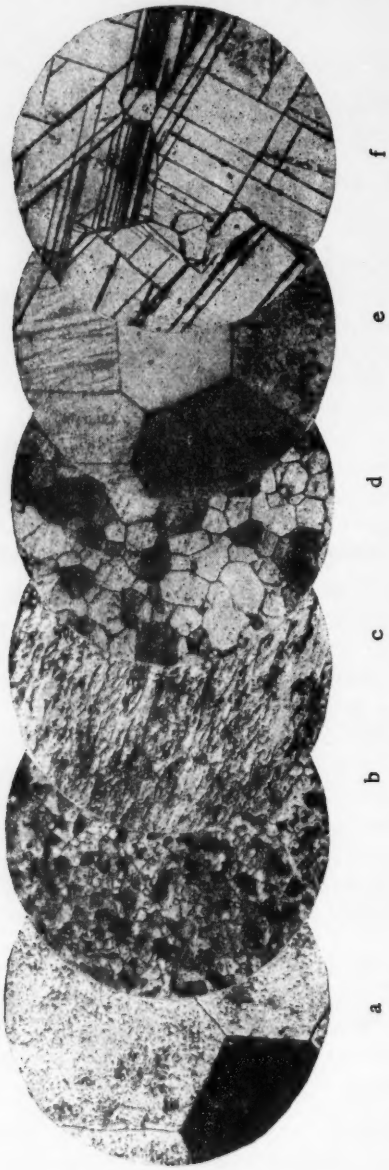

Fig. 2. Microstructure of tantalum (200×). a) Cast; b) initial structure, annealed at 1300° for 2 hours after forging; c) 67.6% deformation by cold rolling; d) 67.6% deformation, annealed at 1800° for 1 hours; e) 67.6% deformation, annealed at 2000° for 1 hour; f) 67.6% deformation, annealed at 2500° for 1 hour.

Lines showing the beginning of recrystallization as a function of the degree of deformation are shown in the recrystallization diagram as broken lines (Fig. 1).

The temperature at which recrystallization of the tantalum began decreased from 1300 to 1200° as the degree of deformation increased. At a deformation 2.6%, recrystallization began at a temperature of 1300°; the temperature was 1275° at 10-34%; it decreased to 1250° at 50-68%; and it reached 1200° at 84% and higher. In Fig. 3 are presented some x-ray patterns of tantalum. Cold rolling of tantalum at low degrees of deformation (up to 15%) led to alteration of its lattice and to deformation of the individual grains, but it did not introduce any essential change in the microstructure. A sharply expressed texture of the rolled metal was observed at deformations with degrees of reduction greater than 30% (Fig. 2c). The high plasticity of tantalum caused a sharp change in the form of the individual grains, and was responsible for their elongation without crushing to reductions of ~50-60%; at greater deformation, the grains crushed. The diameter of the grains was 1-2 μ at a deformation of 90%. Annealing at 1000-1600° did not cause appreciable grain growth. The process of recrystallization, during working, at 1200° in samples with a high degree of deformation and at 1600° for all degrees of deformation led to complete disappearance of the rolling texture and to the appearance of new, fine, recrystallized grains with a diameter of the order of 13-6 μ. A sharp change in the grain size, which is connected with the process of 7 aggregates, recrystallization, took place during annealing at 1800 and 2000° (Fig. 2d and 2e). The size of the original grain, which is approximately 10 μ at 1000-1600°, increased three-fold at

Fig. 3. X-ray patterns of tantalum samples; a) 34% deformation of the sample, b) 34% deformation of the sample, annealed at 1275°.

1800° (to 31 μ), and at 2000° it increased by a factor of ten (to 115 μ). Significant grain growth was also observed at different degrees of deformation. Maximum grain sizes, corresponding to critical degrees of deformation, are observed at 1800 and 2000° on the annealing isotherms. At 1800°, the maximum corresponded to a deformation of 8%, and it shifted to a lower degree of deformation (5.7%) with an increase in the annealing temperature to 2000°. On the 2500° isotherm, maximum grain size approached very low degrees of deformation. An interesting fact, which is, apparently, a specific feature of tantalum, was the appearance of annealing twins at 2500° at all degrees of deformation (Fig. 2f), and there was exceptional grain growth at this temperature which changed grain size by several orders of magnitude. The size of the original grain reached 500 μ, and the grain size at 83% deformation was 320 μ. The investigation of recrystallization at higher degrees of deformation with annealing at 2500° continues. An investigation of the effect of the degree of deformation and of annealing temperature on the tensile strength and on the plasticity of tantalum during elongation (using small samples of the Gargarin type with a diameter of 3 mm) and of the effect on hardness showed that tantalum has its optimum properties after annealing at 1300°. (Properties of the cold-deformed tantalum: σ_B = 95 kg/sq. mm δ = 5%; ψ = 45%; after annealing at 1300° σ_B = 60 kg/sq. mm , δ = 22%; ψ = 58%) An increase in annealing temperature to 1600° and higher led to an increase in hardness and in tensil strength with a corresponding decrease in elongation. This phenomenon is connected with the ability of tantalum to absorb gases particularly intensively in the temperature range of 1600-1800° and to its hardening owing to the formation of solid solutions with oxygen [3-5]. Therefore, retention of high plasticity at annealing temperature of the order of 1600° is possible only with the maintainence of a high vacuum. On the basis of the data obtained, the optimum annealing regime, one which guarantees the production of a fine-grained, polyhedral structure and good mechanical properties, can be taken as a temperature of the order of 1300-1400°.

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SYNTHESIS OF OXIDES OF SILICOOLEFINS FROM CHLOROHYDRINS

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The first oxide of a silicoolefin (a γ, δ-secondary-tertiary oxide) was recently prepared [1] by the interaction of a Grignard reagent with epichlorohydrin. The course of the reaction was very complex, and the yields of organosilicon chlorohydrin and oxide did not exceed 25-30%.

In the present investigation, we established that the interaction of monochloroacetone with Grignard reagents prepared from silicon halides $\left[\begin{array}{l}\diagdown\\ -\mathrm{Si}-(\mathrm{CH_2})_n\mathrm{MgX}\\ \diagup\end{array}\right]$ proceeds unilaterally, which makes it possible to prepare tertiary-primary β, γ- and δ, ϵ-oxides in yields of 80-90% according to the scheme:

$$\text{I. } \mathrm{R_3Si[CH_2]}_n\mathrm{MgX} + \mathrm{CH_3COCH_2Cl} \longrightarrow \mathrm{R_3Si[CH_2]}_n-\underset{\mathrm{CH_3}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{Cl},$$

$$\text{II. } \mathrm{R_3Si(CH_2)}_n-\underset{\mathrm{CH_3}}{\mathrm{C}}\,|\,\mathrm{OH}\,|-\mathrm{CH_2}-\mathrm{Cl} \xrightarrow{\mathrm{NaOH}} \mathrm{R_3Si}-\mathrm{[CH_2]}_n-\underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\mathrm{C}}}-\mathrm{CH_2}.$$

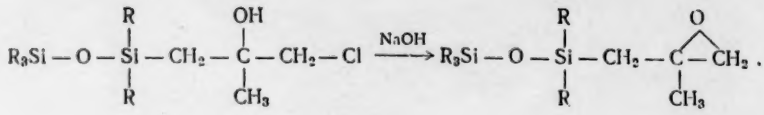
It is interesting to note that, in contrast to γ, δ- and δ, ϵ-halohydrins, β, γ-halohydrins do not yield oxides under the influence of NaOH: rather, they give unsaturated halides in quantitative yield, the halides being formed according to the equation:

$$\mathrm{R_3Si}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\mathrm{C}}(\mathrm{OH})-\mathrm{CH_2}-\mathrm{Cl} \xrightarrow{\mathrm{NaOH}} \mathrm{R_3Si}-\mathrm{CH_2}-\underset{\mathrm{CH_2}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{Cl}+\mathrm{H_2O}.$$

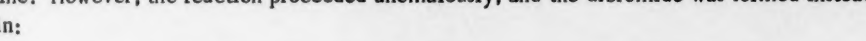
We were able to direct the course of the reaction toward the formation of oxides either by substituting $Ca(OH)_2$ for NaOH, the reaction proceeding according to :

$$\mathrm{R_3Si}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\mathrm{C}}(\mathrm{OH})-\mathrm{CH_2}-\mathrm{Cl} \xrightarrow{\mathrm{Ca(OH)_2}} \mathrm{R_3Si}-\mathrm{CH_2}\overset{\mathrm{O}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}$$

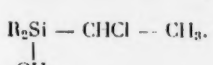
or by substituting R_3SiO for an alkyl radical R, the reaction proceeding according to:



An attempt was made to prepare an α,β-bromohydrin by the addition of hypobromous acid to triethylvinylsilane. However, the reaction proceeded anomalously, and the dibromide was formed instead of the bromohydrin:

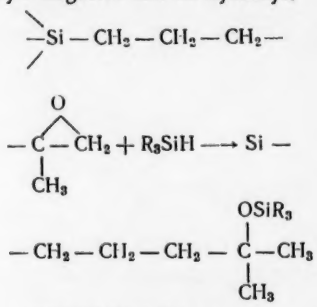


I. N. Nazarov and A. A. Akhrem [2] recently observed a similar anomalous addition of HOBr by 1-vinyl-1-cyclohexanol, which also formed a dibromide, while the bromohydrin was obtained from the corresponding acetate. An unsuccessful attempt was also made to prepared an oxide from:



Here, under the influence of NaOH, hydrolysis of the Si—C bond occurred with the formation of $R_2Si(OH)_2$, while under the influence of $Ca(OH)_2$, the original compound was not converted, but was recovered unchanged.

A δ,ε-oxide also readily adds a silane containing a Si—H bond with the formation of an ether (and not an alcohol), a fact which was established by a negative test for hydroxyl:



EXPERIMENTAL

3-Trimethylsilyl-1-chloro-2-methyl-2-propanol (I). To a Grignard reagent prepared from 24 g (1 mole) of magnesium and 122.5 g (1 mole) of α-chloromethyltrimethylsilane in 400 ml of absolute ether was added dropwise 92.5 g (1 mole) of freshly distilled monochloroacetone while stirring and cooling with ice. The contents of the flask were then stirred for about an hour at room temperature, and were then heated on a water bath for 2 hours. The resulting yellow product was decomposed with ice and 3% HCl. The ether layer was separated, washed twice with a 3% solution of Na_2CO_3 and then with water, and dried over Na_2SO_4. After distillation of the ether, the reaction product was distilled under vacuum at 4 mm Hg. Fractionation I, 25 g, boiled at 45-59°; Fraction II, 120 g, boiled at 59-60°; the residue (a tar) amounted to about 13 g.

The following were prepared in an analogous manner: 3-dimethylsilyl-1-chloro-2-methyl-2-propanol (II), 3-methyldiethylsilyl-1-chloro-2-methyl-2-propanol (III), 3-pentamethylsiloxanyl-1-chloro-2-methyl-2-propanol (IV), 5-dimethylethylsilyl-1-chloro-2-methyl-2-pentanol (V), 5-methyldiethylsilyl-1-chloro-2-methyl-2-pentanol (VI). The properties of these compounds and their yields are presented in Table 1.

5-Dimethylethylsilyl-2-methyl-1,2-epoxypentane (VII). 80 g of finely powdered NaOH, 250 ml of dry ether, and 110 g (0.58 mole) of V were placed in a 500-ml round-bottomed flask fitted with a reflux condenser. The contents of the flask were heated for 6 hours at the boiling point of ether, and were then allowed to stand

TABLE 1

Compound No.	Formula	B.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield %	C, % found	C, % calc.	H, % found	H, % calc.	Si, % found	Si, % calc.	Cl, % found	Cl, % calc.	OH, % found	OH, % calc.
I	$CH_3 \cdot Si(CH_3)-CH_2-C(CH_3)(OH)-CH_2Cl$	59—60	4	1.4541	0.9693	50.50	50.05	70.0	46.61 46.60	46.54	9.32 9.30	9.42	15.25 15.49	15.52	18.75 18.95	19.68	1.07 1.02	1.0
II	$CH_3 \cdot C_2H_5 \cdot Si-CH_2-C(CH_2)(OH)CH_2Cl$	68—69	3	1.4600	0.9676	55.14	55.19	70.0	49.76 49.69	49.36	10.16 9.97	9.77	14.17 14.53	14.40	17.56 17.34	18.25		
III	$CH_3(C_2H_5)_2SiCH_2-C(CH_3)(OH)CH_2Cl$	95.0	5	1.4610	0.9323	61.46	59.82	50	—	—	—	—	—	—	—	—	0.920 1.14	1.01
IV	$CH_3 \cdot Si(CH_3)_2-O-Si(CH_3)_2-CH_2-C(CH_3)(OH)-CH_2-Cl$	67—67.5	1	1.4380	0.9666	69.23	69.20	75	—	—	—	—	—	—	—	—	1.06 1.03	1.0
V	$CH_3 \cdot C_2H_5 \cdot Si-CH_2-CH_2-CH_2-C(CH_3)(OH)-CH_2Cl$	95—95.5	1	1.4570	0.9316	65.14	64.45	50	54.42 54.38	53.93	10.44 10.43	10.34	12.42 12.55	12.55	14.74 15.03	15.96	1.09 1.09	1.01
VI	$CH_3 \cdot C_2H_5 \cdot Si-CH_2-CH_2-CH_2-C(CH_3)(OH)-CH_2Cl$	104—105	2	1.4635	0.9450	69.09	69.08	55	55.75 55.89	55.81	10.63 10.55	10.57	11.91 12.00	11.84	14.40 14.27	15.01	1.03 1.01	1.01

TABLE 2

Compound No.	Formula	B. p.,°C	Pressure, mm, Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield %	C, % found	C, % calc.	H, % found	H, % calc.	Si, % found	Si, % calc.
VII	$CH_2{:}\ C_2H_5\ SiCH_2{-}CH_2{-}CH_2{-}C(O)CH_2$ (CH_3)	207.5	755	1.4382	0.8484	57.67	57.70	80	64.25 64.21	64.45	11.60 11.81	11.87	15.17 15.08	15.07
VIII	$CH_3\ C_2H_5{:}\ SiCH_2{-}CH_2{-}CH_2{-}C(O)CH_2$ (CH_3)	85—86	3	1.4452	0.8581	62.18	62.33	90	64.88 64.88	65.70	11.93 11.85	12.07	14.89 14.76	14.01
IX	$CH_3{:}SiO{-}Si(CH_3)_2{-}CH_2{-}C(O)CH_2$ (CH_3, CH_3)	71—71.5	10	1.4160	0.8773	62.48	62.45	90	49.41 49.50	49.54	10.03 9.99	10.09	25.59 25.94	25.68
X	$CH_3{:}Si{-}CH_2{-}C(O)CH_2$ (CH_3, CH_3)	67.0	10	1.4243	0.8338	44.18	43.81	52	58.01	58.30	10.93	11.11	18.89	19.44
XI	$CH_2{:}\ C_2H_5\ {-}Si{-}CH_2{-}C(O)CH_2$ (CH_3)	154.0	750	1.4393	0.8539	48.77	48.44	49	—	—	—	—	17.91	17.82

for 12 hours; the reaction mixture was then filtered. After the ether was distilled, the reaction product was distilled in a column. 75 g of product, b. p. 85-85.5°/10 mm, was obtained.

The following were similarly prepared: 5-methyldiethylsilyl-2-methyl-1,2-epoxypentane (VIII), 3-pentamethyldisiloxanyl-2-methyl-1,2-epoxypropane (IX), and, under the influence of $Ca(OH)_2$, the trialkylsilyl-1,2-epoxypropanes X and XI; the properties and yields of these compounds are presented in Table 2.

2-Chloromethyl-3-methyldiethylsilyl-1-propene (XII). 60 g of NaOH, 200 ml of dry ether, and 120 g of β, γ-chlorohydrin (III) were used; the contents of the flask were refluxed for 6 hours. 75 g of product was isolated; b. p. 205°/750 mm; n_D^{20} 1.4635, d_4^{20} 0.9085; $MR_{D\,found}$ 57.87; $MR_{D\,calculated}$ 57.80; 90% yield.

Found %: C 59.99, 57.16; H 10.12, 10.20; Si 15.29, 15.09. $C_9H_{19}SiCl$. Calculated %: C 56.69; H 9.97; Si 14.70.

Raman spectrum (cm^{-1}): 242 (1 b), 380 (0), 455 (0), 484 (4), 527 (1), 580 (6 b), 646 (0 b), 665 (0 b) 698 (1 b), 752 (1 b), 802 (0), 874 (0), 970 (3), 1013 (4), 1108 (5), 1132 (2), 1158 (5 b), 1178 (3), 1194 (0), 1228 (2 b), 1250 (1 b), 1302 (4), 1376 (3), 1406 (3), 1436 (1), 1460 (4), 1631 (10), 2875 (8 b), 2908 (8b), 2954 (6 b), 3070 (2 b).

A frequency was found which is encountered in organosilicon compounds having a branched multiple bond structure, namely: the frequencies 1158, 1302, 1406, 1631, and 3070 cm^{-1}, which permits the assumption that the compound prepared had the structure $CH_3(C_2H_5)_2Si-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2Cl$.

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* Original Russian pagination. See C. B. Translation.

ISOTOPE EXCHANGE OF CO_2 CHEMISORBED ON IRON AMMONIA-SYNTHESIS CATALYST

Iu. E. Siniak, Active Member AN SSSR S. Z. Roginskii and M. I. Ianovskii

The catalytic synthesis of ammonia from nitrogen and hydrogen over iron catalyst promoted with aluminum and potassium has been the subject of a great number of investigations; however, the nature of the promoting action of these promoters remains obscure up to the present.

In a paper by one of us [2], the use of measurements of the isotope exchange rate of atoms on the catalyst surface with the gases was emphasized as one of several possible applications of isotopes to the investigation of catalysts. In comparison with the differential isotope method, previously proposed for the study of heterogeneity [1, 3-5], the kinetic isotope method has a number of advantages, since the probability of the redistribution of molecules is reduced by its use, and since all measurements are carried out without changing the filling of the surface, this last being very essential.

The first studies of the isotope exchange rate of carbon monoxide chemisorbed on the surface of an iron ammonia-synthesis catalyst were carried out by Eischens [6]. In his experiments, the rate constant for the exchange of chemisorbed $C^{14}O$ with $C^{12}O$ of the gas phase gradually dropped, which is impossible to explain as being a reaction effect in view of the constancy of filling of the surface under the experimental conditions used. The author was led to the conclusion that the regions of chemisorbed CO were heterogeneous. Similar results were obtained by N. P. Keier [7], who studied isotope exchange by acetylene over a nickel catalyst. The exchange kinetics satisfied the bilogarithmic relationship characteristic of extensively heterogeneous surfaces with an exponential distribution of regions according to activation energy.

The kinetics of isotope exchange over doubly promoted iron ammonia-synthesis catalyst was investigated in the present work.

EXPERIMENTAL

The work was carried out at 21° with doubly promoted iron ammonia-synthesis catalyst reduced and passivated outside the reaction system.* The composition of the catalyst was (in percent): FeO, 27.3; Al_2O_3, 3.94; K_2O, 1.82; CaO, 0.084; MgO, 0.021; SO_3, 0.017; SiO_2, 0.16.

According to data obtained by V. N. Shishkova, the BET surface area of the catalyst was 13 sq. m/g.

The passivated catalyst was placed in a reaction vessel and reduced in a current of pure hydrogen for 2 hours at 500° and a space rate of 15,000.

The radioactive carbon dioxide was prepared from $BaC^{14}O_3$ and 96% H_2SO_4. The gas obtained was frozen in a liquid nitrogen trap, and the uncondensed gas was pumped out to a pressure of 10^{-4} mm Hg. The purification system consisted of a silica gel column, a dry ice trap, and a P_2O_5 trap.

The inactive carbon dioxide was prepared by pyrolytic decomposition of sodium bicarbonate, and was purified in the same manner.

A diagram of the experimental apparatus is shown in Fig. 1. The essential part of the system comprised a quartz reactor (1) in which was placed a known weight of catalyst (4.1 g), a counting cell(2) and a magnetic circulating pump(3).

*Passivation of the catalyst was carried out by the method described by M. I. Temkin.

The work was carried out as follows. A portion of active $C^{14}O_2$ was started over a previously standardized volume of catalyst. After equilibrium had been established (20 minutes), the unadsorbed $C^{14}O_2$ was frozen out of the circulating system with liquid nitrogen. Preliminary experiments showed that the adsorptive capacity of the sample of catalyst for CO_2 was 3.24 ml (STP). Inactive CO_2 was then fed to the system to a pressure of 100 mm (41 ml), and the circulating pump was switched on. The change in the isotope composition of the gas phase was recorded by means of an MST-17 end-window counter installed in the counting cell. In order to keep the mica window of the counter from being pulled in by the vacuum (window thickness 4.5 mg/sq. cm.), a special glass grid was used. A correction for self-absorption in the gas phase and, in the case of high activity, one for resolving time were introduced into the counter reading.

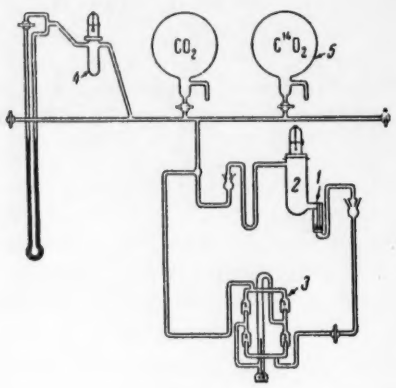

Fig. 1. Simplified diagram of the experimental apparatus; 1) reactor, 2 and 4) counting cells with end-window counters, 3) magnetic circulating pump, 5) storage flasks for the gases.

The direct and continuous measurement of the isotope composition of the gas phase used in the present work has an advantage over the previous method of sample collection and conversion to active $BaC^{14}O_3$. In the present work, it was possible to carry out measurements over a short time interval with high accuracy. In the future, it is proposed to record the readings automatically, using for this purpose an integrating counter.

The curves shown below show that the absorbed CO_2 did not desorb in an atmosphere of CO, H_2, and Ar at a pressure of 500 mm Hg. If CO_2 was introduced into the apparatus, a rapid increase in activity was observed in the gas phase. As seen from the curves, 75% of equilibrium activity was reached in the first 3-4 minutes, after which the increase in the activity was very small, and no appreciable change in the activity (A_{Iex}) in the gas phase was registered over approximately 20-25 hours. After equilibrium had been established, the CO_2 was frozen out in the calibrated vessel (4) with an MST-17 counter, and its total activity was determined (A_{Iex}). It was established that A_{Iex} had a value of the order of 40-50% of the total amount of adsorbed $C^{14}O_2$. After this, the same amount of inactive CO_2 was passed repeatedly over the catalyst. The activity (A_{IIex}) in the gas phase increased insignificantly. This determination was repeated once more. No increase in the activity (A_{IIIex}) in the gas phase could be detected. The reactor was then heated to 475°. The heating caused the appearance in the gas phase of an activity (A_{IV}), which comprised approximately 20% of the total activity of the gas adsorbed by the catalyst. Only the introduction of hydrogen at 475° into the circulation system permitted recovery of the remaining activity. We have been unable to establish the chemical composition of the gases liberated on heating and on treatment of the catalyst with hydrogen at a temperature of 475-500°.

The stages of the kinetic experiment just described are represented in Fig. 2. Similar experiments were carried out repeatedly, and the nature of the changes was readily reproducible.

In another series, the experiments were carried out as follows. A specific amount of inactive CO_2 (1.64 cc STP) was first adsorbed on the conditioned catalyst; this was followed by an accurately measured portion (0.82 cc STP) of active $C^{14}O_2$ after which the usual kinetic experiment was carried out. In another experiment, the same amount (0.82 cc STP) of active $C^{14}O_2$ was adsorbed on the catalyst immediately after conditioning the catalyst, and the isotope exchange curve was determined subsequently (Fig. 3).

As seen from Fig. 3, the per cent exchange depends on the adsorption sequence; if active $C^{14}O_2$ is adsorbed first, the percentage exchange is 15-20% lower than when the reverse is the case.

The fraction of CO_2 exchanged depends not only on the adsorption sequence, but also on the degree of filling of the active regions.

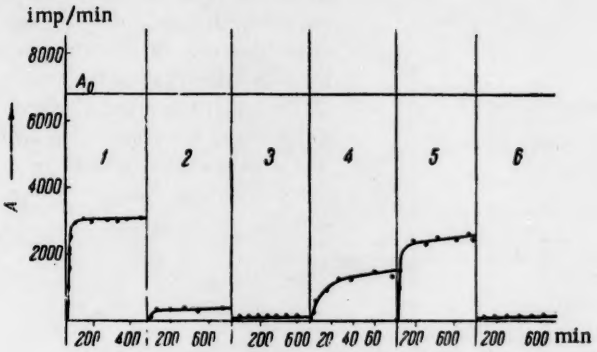

Fig. 2. Transfer of chemisorbed CO_2 into the gas phase under various conditions. 1, 2, and 3) Treatment of the catalyst with three successive portions of inactive CO_2; 4) catalyst heated at a temperature of 475°; 5 and 6) two successive treatments of the catalyst with hydrogen at a temperature of 475°.

In Fig. 4 are presented the results of measurements of the exchange rate of CO_2 in experiments in which 2.85 cc of inactive CO_2 was preliminarily adsorbed on the catalyst and only 0.42 ml of active $C^{14}O_2$. In this case, the percentage exchange was about 60-65%. These data indicate the presence of two regions differing sharply in properties and characteristic of the alkaline part of the catalyst surface. Apparently we are dealing here either with the existence of at least two chemically differing forms of the alkaline promoter or with the presence of a collection of regions differing sharply in their activity. A broad investigation of a large number of ammonia-synthesis catalysts promoted differently would permit a deeper penetration into the question of the promoting action of alkaline promoters and of the role of CO_2 as a catalyst poison.

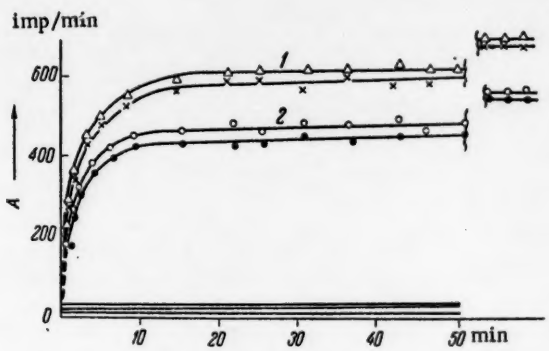

Fig. 3. Relationship between isotope exchange rate and order of filling of the catalyst surface. 1) 1.64 ml of inactive CO_2 adsorbed first, and 0.82 ml of active $C^{14}O_2$ then introduced; 2) active $C^{14}O_2$ adsorbed immediately after conditioning of the catalyst.

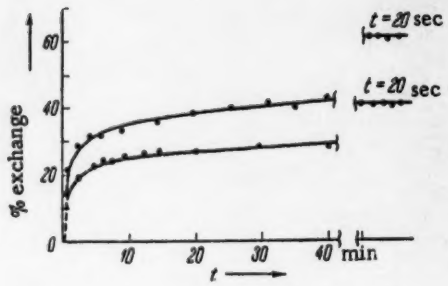

Fig. 4. Variation in isotope exchange rate and degree of preliminary filling of the surface with inactive CO_2.

The absence of a transfer of activity during lengthy circulation in an atmosphere of CO, H_2, and Ar and the rapid exchange with CO_2 present in the gas phase indicate that, in the present case, the mechanism of the exchange apparently approaches that proposed by some authors [8] for the process of the exchange of CO_2 in alkali metal and alkaline earth metal carbonates. According to this scheme, the first stage is the adsorption of gas on the surface of the carbonate with formation of a surface compound between the adsorbed dioxide with the carbonate

$$[C^{14}O_3^{2-} \cdot C^{12}O_2] \rightleftarrows [C^{12}O_3 \cdot C^{14}O_2]$$

with subsequent desorption of $C^{14}O_2$ into the free space; i.e., a double exchange proceeds with the formation of an intermediate complex rather than a dissociation exchange through the gas phase.

The authors express their deep appreciation to I. P. Sidorov and S. S. Lachinov for the gift of the catalysts and for a number of valuable suggestions during the course of the work.

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SYNTHESIS AND PROPERTIES OF PHENYL-, 3,4-XYLYL- AND 4-ISOPROPYLPHENYLALKYLSILANES

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In recent years, considerable attention has been given to the synthesis and study of the physicochemical and technical properties of silicohydrocarbons of various structures. Silicohydrocarbons containing aryl and alkyl radicals joined to the silicon atom – arylalkylsilanes – are of great interest.

We have described mono-, di-, and tri-p-tolylalkylsilanes in a previous communication [1]. In the present article, the preparation and properties of phenylalkylsilanes, 1-(3,4-xylyl)alkylsilanes, and 1-(4-isopropylphenyl)alkylsilanes are described.

Of the 1-(3,4-xylyl)alkylsilanes, only one, 1-(3,4-xylyl)trimethylsilane [2], is known. 1-(4-isopropylphenyl)alkylsilanes have not been described in the literature.

We synthesized the phenylalkylsilanes for the purpose of comparing their physicochemical properties with those of the other arylalkylsilanes.

A number of the phenylalkylsilanes were prepared for the first time.

All of these phenylalkylsilanes were prepared by means of organomagnesium and organolithium compounds.

The 1-(3,4-xylyl)alkylsilanes (Table 1) were prepared by the interaction of 3,4-xylyllithium with the appropriate alkylhalo- or alkylethoxysilanes. The 3,4-xylyllithium was prepared from 4-bromo-o-xylene, which, in turn, was prepared by bromination of o-xylene. 4-Bromoisopropylbenzene was similarly prepared and converted to the lithium derivative, from which di(4-isopropylphenyl)dimethylsilane and di(4-isopropylphenyl)-diethylsilane were prepared.

The physicochemical properties of the phenyl-, the 3,4-xylyl-, and the 4-isopropylphenylalkylsilanes are presented in Table 1.

Phenyltrimethylsilane. 108 g of trimethylchlorosilane was added to phenylmagnesium bromide prepared from 48 g of magnesium and 318 g of bromobenzene. The mixture was heated 18 hours. 62 g (41.3% yield) was obtained.

Phenyltriethylsilane. 105 g of phenyltrichlorosilane was added to ethylmagnesium bromide prepared from 72 g of magnesium and 328 g of ethyl bromide. The mixture was heated 15 hours. 78 g (81.5% yield) was obtained.

Phenyltripropylsilane. 105 g of phenyltrichlorosilane was added to propylmagnesium bromide prepared from 72 g of magnesium and 366 g of propyl bromide. The mixture was heated 15 hours. 80 g (68.5% yield) was obtained.

Phenyltributylsilane. 105 g of phenyltrichlorosilane was added to butylmagnesium bromide prepared from 72 g of magnesium and 411 g of butyl bromide. The mixture was heated 15 hours. 70 g (50.7% yield) was obtained.

Diphenyldimethylsilane. 64.5 g of dimethyldichlorosilane was added to phenylmagnesium bromide prepared from 24 g of magnesium and 157 g of bromobenzene. The mixture was heated 12 hours. 83.5 g (78.9% yield) was obtained.

TABLE 1

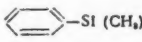
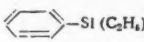
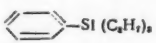
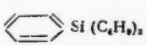
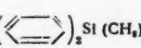
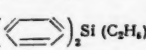
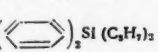
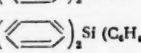
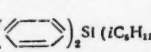
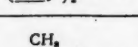
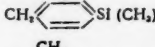
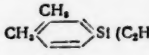
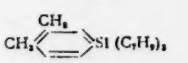
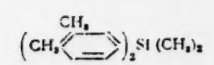
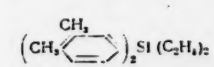
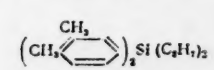
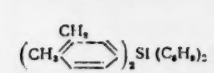
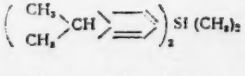
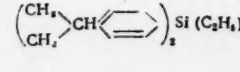
Compound	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found % C	Found % H	Calc. % C	Calc. % H
Phenyltrimethylsilane [3]		65/20	0.8722	1.4908	49.88	49.95	—	—	—	—
Phenyltriethylsilane [4]		93—94/5	0.8915	1.5003	63.48	63.84	—	—	—	—
Phenyltripropylsilane		127—129/9	0.8799	1.4950	77.01	77.73	76.82 76.73	11.22 11.13	76.88	11.18
Phenyltributylsilane		140—142/4	0.8753	1.4915	91.42	91.62	78.25 78.09	11.64 11.62	78.17	11.59
Diphenyldimethylsilane [5, 6]		113—115/4	0.9898	1.5628	69.67	69.62	—	—	—	—
Diphenyldiethylsilane [7]		134—135/3	0.9844	1.5600	78.96	78.88	—	—	—	—
Diphenyldipropylsilane		142—144/4	0.9651	1.5476	88.31	88.22	80.77 80.60	9.09 9.10	80.55	9.01
Diphenyldibutylsilane		149—152/3	0.9523	1.5404	97.74	97.40	81.05 81.00	9.48 9.48	81.01	9.51
Diphenyldiisoamylsilane		180—182/5	0.9404	1.5338	107.24	106.66	81.81 81.87	10.12 10.13	81.45	9.93
1-(3,4-xylyl)trimethylsilane [8]		73—75/6	0.8754	1.4998	59.89	59.21	—	—	—	—
1-(3,4-xylyl)triethylsilane		115—117/4	0.8963	1.5003	73.57	73.29	76.27 76.27	11.19 11.04	76.27	10.98
1-(3,4-xylyl)tripropylsilane		145—147/6	0.8829	1.5020	87.76	87.02	77.38 77.39	11.53 11.49	77.79	11.50

TABLE 1 (continued)

Compound	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found % C	Found % H	Calculate % C	Calculate % H
1-(3,4-dixylyl)tributylsilane		155—156/4	0.8783	1.4980	101.66	100.88	78.98 79.00	11.97 11.84	78.88	11.92
Di(3,4-xylyl)dimethylsilane		m.p. 54.5—55.5	—	—	—	—	80.62 80.76	9.03 9.06	80.55	9.01
Di(3,4-xylyl)diethylsilane		161—162/3	0.9705	1.5595	98.71	97.40	80.80 80.91	9.46 9.56	81.01	9.51
Di(3,4-xylyl)dipropylsilane		187—188/4	0.9533	1.5352	106.60	106.66	81.63 81.55	10.02 10.03	81.41	9.95
Di(3,4-xylyl)dibutylsilane		m.p. 41—42	—	—	—	—	82.04 82.27	10.25 10.36	81.75	10.30
Di(4-isopropylphenyl)dimethylsilane		167—168/4	0.9428	1.5370	98.21	97.40	81.12 81.04	.63 9.48	81.01	9.51
Di(4-isopropylphenyl)diethylsilane		173—174/3	0.9474	1.5410	107.04	106.66	81.58 81.57	9.94 9.77	81.45	9.93

Diphenyldiethylsilane. 127 g of diethyldichlorosilane was added to phenylmagnesium bromide prepared from 84 g of magnesium and 471 g of bromobenzene. The mixture was heated 15 hours. 95 g (49% yield) was obtained.

Diphenyldipropylsilane. 41 g of dipropyldiethoxysilane was added to phenyllithium prepared from 6 g of lithium and 65 g of bromobenzene. The mixture was heated 8 hours. 17.8 g (35% yield) was obtained.

Diphenyldibutylsilane. 20 g of dibutyldiethoxysilane was added to phenyllithium prepared from 3.5 g of lithium and 37 g of bromobenzene. The mixture was heated 8 hours. 15.8 (54% yield) was obtained.

Diphenyldiisoamylsilane. 18 g of diisoamyldiethoxysilane was added to phenyllithium prepared from 2.5 g of lithium and 23.9 g of bromobenzene. The mixture was heated 10 hours. 9.7 g (43% yield) was obtained.

1-(3,4,-Xylyl)trimethylsilane. 43.2 g of trimethylchlorosilane was added to 3,4-xylyllithium prepared from 6 g of lithium and 76 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 41.5 g (57.7% yield) was obtained.

1-(3,4-Xylyl)triethylsilane. 40 g of triethylbromosilane was added to 3,4-xylyllithium prepared from 2.5 g of lithium and 33 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 21 g (46% yield) was obtained.

1-(3,4-Xylyl)tripropylsilane. 42.8 g of tripropylethoxysilane was added to 3,4-xylyllithium prepared from 2.8 g of lithium and 37 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 30 g (57% yield) was obtained.

1-(3,4-Xylyl)tributylsilane. 36.2 g of tributylethoxysilane was added to 3,4-xylyllithium prepared from 2.5 g of lithium and 30 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 15.5 g (33% yield) was obtained.

Di(3,4-xylyl)dimethylsilane. 28.2 g of dimethyldichlorosilane was added to 3,4-xylyllithium prepared from 8.4 g of lithium and 92.5 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 40.5 g (69% yield) was obtained.

Di(3,4-xylyl)diethylsilane. 32 g of diethyldichlorosilane was added to 3,4-xylyllithium prepared from 6.9 g of lithium and 83 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 38.5 g (68.5% yield) was obtained.

Di(3,4-xylyl)dipropylsilane. 18 g of dipropyldichlorosilane was added to 3,4-xylyllithium prepared from 3 g of lithium and 39 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 16.5 g (51% yield) was obtained.

Di(3,4-xylyl)dibutylsilane. 50 g of dibutyldiethoxysilane was added to 3,4-xylyllithium prepared from 7 g of lithium and 92 g of 4-bromo-o-xylene. The mixture was heated 8 hours. 33 g (40% yield) was obtained.

Di(4-isopropylphenyl)dimethylsilane. 26 g of dimethyldichlorosilane was added to 4-isopropylphenyllithium prepared from 5.6 g of lithium and 79.6 g of 4-bromoisopropylbenzene. The mixture was heated 8 hours. 36 g (61% yield) was obtained.

Di(4-isopropylphenyl)diethylsilane. 33 g of diethyldichlorosilane was added to 4-isopropylphenyllithium prepared from 7 g of lithium and 90 g of 4-bromoisopropylbenzene. The mixture was heated 8 hours. 50.7 g (73.6% yield) was obtained.

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CONTRIBUTION TO THE PROBLEM OF THE THERMODYNAMICS OF THE HYDROCHLORINATION OF ISOBUTYLENE

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Hydrochlorination reactions of unsaturated hydrocarbons are equilibrium reactions, and thermodynamic calculation of these reactions are not only of theoretical interest, but are also of practical interest for the selection of optimum process conditions. In particular, the thermodynamic calculation of the hydrochlorination of isobutylene merits attention. The equilibrium of this reaction was first studied experimentally by Kistiakowsky and Staufer [1], who, on the basis of the equilibrium composition of the gases, calculated the equilibrium constants and the free energy changes of the reaction for a narrow temperature interval. They proposed a linear equation for ΔF_T^0, and extrapolation over a broad temperature interval without verification by more rigorous calculation would appear to be hazardous.

More recently, B. A. Krentsel' and N. A. Pokotilo [2] studied the catalytic hydrochlorination of butenes over solid catalysts. In their work, attention was devoted primarily to an experimental determination of optimum reaction conditions. Recently, S. G. Entelis [3] investigated the kinetics of the hydrochlorination of isobutylene on films of acid catalysts. He also proposed an approximate linear equation for the determination of the equilibrium constant.

We now present a more rigorous thermodynamic calculation of the hydrochlorination of isobutylene, using molecular and spectral data for tertiary butyl chloride.

TABLE 1

Atomic Coordinates (in A)

	x	y	z
Cl	0	0	+1.334
C_3	0	0	−0.436
C_1	+1.466	0	−0.910
H_{11}	+2.126	0	−0.043
H_{12}	+1.653	+0.890	−1.510
H_{13}	+1.653	−0.890	−1.510
C_2	−0.733	+1.271	−0.910
H_{21}	−1.063	+1.841	−0.043
H_{22}	−1.597	+0.987	−1.510
H_{23}	−0.056	+1.877	−1.510
H_1	−0.733	−1.271	−0.910
H_{31}	−1.063	−1.841	−0.043
H_{32}	−1.597	−0.987	−1.510
H_{33}	−0.057	−1.877	−1.510

The molecule of tertiary butyl chloride has C_{3v} symmetry. It can be considered as a C−Cl frame to which are attached three symmetrical tops $-CH_3$. We used the following data for the calculation of the functions associated with translational motion, rotation, and torsional vibration: C−H distance = 1.09 A, C−C distance = 1.54A, Cl−C−C angle = 111°, and the H−C−H angle was taken as tetrahedral. Since rotation of the methyl groups does not change the principal moments of inertia of molecules, we used a "shaded" model of the molecule; i.e., one C−H bond was considered to lie in a plane with a C−C bond. With these angles and interatomic distances, the atomic coordinates have the values shown in Table 1; the $\underline{z}$ axis coincides with the direction of the C−C bond. These data give the following values for the principal moments of inertia of the entire molecule: $I_X = I_y = 26.77 \cdot 10^{-39}$ g·cm², $I_Z = 18.65 \cdot 10^{-39}$ g·cm². The product of the principal moments of inertia is $I_X I_y I_Z = 1.400 \cdot 10^{-113}$.

The value of the molecular weight (92.569) and the product of the principal moments of inertia permit calculation of the translational and rotational contributions to entropy, free energy, and other thermodynamic functions as functions of temperature for one mole of the gas. The following equations were used for entropy and free energy:

TABLE 2

Values of the Thermodynamic Functions of Tertiray Butyl Chloride

T, °K	298.16	300	400	500	600	700	800	900	1000
1. Translational and rotational (free internal rotation) contributions									
S°_T, cal.	74.367	74.434	77.579	80.016	82.009	83.684	85.154	86.442	87.593
$-\frac{F^\circ_T - E^\circ_0}{T}$	63.437	63.504	66.649	69.086	71.073	72.654	74.224	75.512	76.663
$C_P = 4R$	7.949								
$\frac{U^\circ_T - E^\circ_0}{T}$	10.93								
2. Vibtational contributions									
S°_T, cal.	7.266	7.344	11.991	17.131	22.066	27.071	31.766	36.625	41.163
$-\frac{F^\circ_T - E^\circ_0}{T}$	2.302	2.351	4.160	6.334	8.453	10.737	13.075	15.461	17.700
C_{cal}	13.072	13.218	19.407	26.056	30.367	34.420	38.128	41.344	43.992
3. Contribution of restricted internal rotation (Y = cal./mole)									
$3(S^\circ_f - S^\circ)$	2.562	2.562	1.731	1.215	0.909	0.675	0.546	0.438	0.335
$-3\frac{F^\circ_T - F}{T}$	3.948	3.948	3.489	3.081	2.760	2.457	2.205	2.022	1.908
$3z$	6.156	6.156	5.553	4.965	4.311	4.203	3.972	3.789	3.636
4. Final values of the thermodynamic functions (Y = 2000 cal./mole)									
S°_T	79.1	79.2	87.8	95.9	103.2	110.1	116.4	122.7	128.4
$-\frac{F^\circ_T - E^\circ_0}{T}$	61.8	61.9	67.3	72.3	76.8	80.9	85.1	89.0	92.5
$\frac{U^\circ_T - E^\circ_0}{T}$	17.3	17.3	20.5	23.6	26.4	29.2	31.2	33.7	36.0
C°_P	27.18	27.33	32.91	38.97	42.63	46.57	50.05	53.08	55.58
$-(F^\circ_T - E^\circ_0)$	18 420	18 570	26 930	36 170	46 060	56 650	68 080	80 060	92 460
$U^\circ_T - E^\circ_0$	5160	5190	8210	11 800	15 840	19 710	25 020	30 310	36 000
F°_T	−55 580	−55 730	−64 090	−73 330	−83 220	−93 810	−105 240	−117 220	−129 620
U°_T	− 3200	−31 970	−28 950	−25 370	−21 320	−17 450	− 12 140	− 6840	−1250
ΔF°_T, kcal.	−15.346	−15.2	+ 5.6	+ 4.3	+14.6	+24.3	+ 35.2	+ 45.9	+ 56.5
ΔH°_T kcal.	−43.200	−43.3	−44.8	−46.0	−47.7	−48.5	− 48.7	− 48.8	49.0
ΔS°_T	−93.44	−93.7	−98.0	−100.7	−102.7	−103.9	−104.9	−105.2	−105.5
5. Final values of the thermodynamic functions (Y = 3000 cal./mole)									
$3(S^\circ_f - S)$	4.008	3.987	2.979	2.253	1.740	1.474	1.200	1.020	0.840
$-3\frac{F^\circ_T - E^\circ_0}{T}$	5.019	5.013	4.602	4.239	3.789	3.483	3.189	2.898	2.664
ΔF°_T kcal.	−14.8	−14.6	−5.0	+4.8	+15.3	+24.4	+35.9	+46.6	+57.4

$$S_T^0(\text{trans.} + \text{rot.} \quad) = 25.1663\log T + 19.094, \tag{1}$$

$$-\frac{F_T^0 - E^0}{T} = 25.1663\log T - 1.164. \tag{2}$$

The frequency assignments for tertiary butyl chloride are available in the literature [4]. The missing vibrational frequency of the methyl group (A_2) was taken as 960 cm^{-1} in analogy to other compounds. Thus in the cited work, the following frequencies were assigned: 304(2), 570, 372, 406(2), 812, 925(2), 160, 1026(2), 1147, 1234(2), 1361(3), 1445 (6), 2950(9). On the basis of these assignments and Equations (1) and (2), the values of the thermodynamic functions associated with translational, all rotational (including the symmetrical top CH_3), and vibrational motions of the molecule were calculated.

TABLE 3

T, °K	ΔF_T°	lg K	K	ΔF_T° (Kistiakowsky)	ΔF_T° (Y = 3000 cal./mole)
298.0	−6400	4.675	$4.7 \cdot 10^4$	−6,334	−6.000
300	−6300	4.61	$4.08 \cdot 10^4$		
350	−4500	2.86	730		−4100
400	−2700	1.47	29.7	−2660	−2200
450	−900	0.45	2.78		− 400
500	+800	−0.48	0.33	+950	+1440

The results are presented in Table 2. For calculation of the error due to restricted rotation of the methyl groups (the reduced moment of the model group in the present case is $5.19 \cdot 10^{-40}$ g · cm^2), a restricting potential barrier of 3,000 cal/mole was first chosen.. However, a comparison of the calculated results with the experimental data of Kistiakowsky [1] for the hydrochlorination of isobutylene showed that better agreement is obtained with a potential barrier of 2,000 cal/mole. This value approaches more closely the data of Euken [5] for the potential barrier in ethyl chloride (Y = 2700 cal/mole) than it does to the data of the American authors [6] (Y = 4700 cal/mole). The decrease in the height of the potential barrier in comparison with that of isobutane can be explained both by a decrease in the repulsions of the hydrogen atoms due to the absence of a tertiary hydrogen atom and by an increase in the angle between the C−C bonds to 111°. Therefore, all thermodynamic functions presented in Table 2 were calculated using a potential barrier of 2,000 cal/mole. Nevertheless, corrections for a potential barrier of 3,000 cal/mole are also presented in the table. Combining the value from Table 2 of $\Delta H^0_{298.16} - E^0_0$ for tertiary butyl chloride with the heats of formation of isobutylene and of hydrogen chloride and with the heat of hydrochlorination of isobutylene (according to Kistiakowsky), $\Delta H^0_{298.16}$ = 17,100 cal/mole, we obtain for tertiary butyl chloride $\Delta H^0_{298.16}$ = − 43206 cal/mole and E^0_0 = 37160 cal/mole (17,160). For confirmation of these values, the free energy change and the equilibrium constants were calculated for the reaction

$$i\text{-}C_4H_8 + HCl \rightleftarrows \text{tert-}C_4H_9Cl.$$

TABLE 4

Composition of Equilibrium Gases

	Temperature, °K									
	298,16		350		400		450		500	
Pressure, atm.	1	20	1	20	1	20	1	20	1	20
i-C_4H_8, %	0.46	0.1	3.56	0.82	15.3	4.0	34.0	11.7	45.4	26.6
HCl, %	0.46	0.1	3.56	0.82	15.3	4.0	34.0	11.7	46.4	26.8
tert-C_4H_9Cl, %	99.08	99.8	92.88	98.36	69.4	92.0	32.0	76.6	6.2	46.4

The data of Kistiakowsky, calculated for 400° K, were used for selection of the height of the potential barrier. The results of the calculations are presented in Table 3, where are also given values of ΔF_T^0 for a potential barrier of 3,000 cal/mole for certain temperatures, these values being calculated from the data of Kistiakowsky. As seen from Table 3, agreement is good for different temperatures in a broad temperature interval (300-1000°). The compositions of the equilibrium mixtures for i-C_4H_8 + HCl in a ratio of 1 : 1 and at pressures of 1 and 20 atm. were calculated at intervals of 50° for the range 300-500° (Table 4). The calculated values are in good agreement with the experimental values indicated above.

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THERMAL AND X-RAY PHASE ANALYSES OF THE SYSTEM $CsF - BeF_2$ AND ITS RELATIONSHIP TO SYSTEMS OF THE TYPE $M^IF - BeF_2$

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In the development of the ideas of Goldschmidt [1] on structural models for complex oxides, studies have been carried out in our laboratories and in laboratories abroad on the systems $M^+F - BeF_2$, which can be regarded as weakened fluoride "models" of systems of the type $M^{2+}O - SiO_2$, where M^+: Li [2-4], Na [4-7]; K [8]; Rb [7-9-11].

From the point of view of the change in stability of different fluoberyllates, considerable interest was attached to a study of the system $CsF - BeF_2$. Differential-thermal and x-ray phase methods of study were adopted.

The starting substances used for the preparation of cesium fluoberyllates and intermediate compositions of the system were Cs_2CO_3, CsCl and $(NH_4)_2BeF_4$.

Four compounds were detected in the system: Cs_3BeF_5; Cs_2BeF_3; $CsBeF_3$; $CsBe_2F_5$. They are all readily prepared by fusing mixtures of the components taken in stoichiometric amounts, while the salts Cs_2BeF_4 and $CsBeF_3$ are also separated from aqueous solution. CsF was prepared by the decomposition of Cs_2CO_3 with hydrofluoric acid and removal of the excess HF by heating to above 600°. When CsCl was used the Cl^- ion was removed with freshly precipitated silver oxide.

The melts for the thermal analysis were prepared from accurately weighed samples of analyzed $CsF \cdot HF$; Cs_2BeF_4; $CsBeF_3$ and BeF_2. Check on the composition of the prepared melts was carried out up to 50% BeF_2 (here and afterwards mole percentages are given) by analysis for cesium, and above 50% by analysis for beryllium. The deviation of the experimental data from the calculated data did not exceed 1% by weight for cesium fluoride and 0.6% by weight for beryllium fluoride.

The melts containing 0, 7; 13, 25, 31.5, 32.4, 33.3, 42.7, 47, 50, 54.7, 60.7, 66.66, 85.4, 90.8 and 100% BeF_2 were studied by x-ray crystallographic methods.

Study of the system in the region from 0-33% BeF_2 proved difficult as a result of the highly hygroscopic nature of the cesium fluoride (in this connection $CsF \cdot HF$, and not CsF, was taken in order to avoid hydrolysis) and the peculiar property of the melts of creeping along the walls of the platinum test tubes used in the thermal analysis. It was only possible to avoid this by reducing the rate of heating, so that part of the diagram (Fig. 1), up to 15% BeF_2, is constructed only from the cooling curves. The remaining part of the diagram is constructed from the heating curves, since on the less sensitive differential cooling curves the effects of polymorphic changes often were not observed. The liquidus curve for the quartz-like beryllium fluoride is less reliable as a result of the extensive glass formation in this region and the resultant indistinctness of the limits of the effects on the differential curves.

A high-temperature x-ray analysis was carried out on the specimens using "Unicam" cameras [12], in capillaries of a special glass containing no silicates, which is stable up to the appearance of the liquid phase, but not above 600°.

The m. p. found for CsF was 688°, which agrees with the literature data [13]. At 14% BeF_2 and 598°, CsF

TABLE 1

Analysis Results for the Starting Materials Used in the Preparation of the Melts

Substance being analyzed	Found, % by weight			Calculated, % by weight		
	Be	Cs	F	Be	Cs	F
CsF·HF	—	79.92 ±0.18	20.03 ±0.06	—	77.32	22.11
BeF_2	19.04 ±0.06	—	—	19.13	—	80.87
Cs_2BeF_4	2.68 ±0.06	74.92 ±0.51	—	2.571	75.77	21.65
$CsBeF_3$	4.91 ±0.01	64.51 ±0.22	—	4.53	66.80	28.67

forms a eutectic with Cs_3BeF_5. Cs_3BeF_5 has a noncongruent melting point at 659°. This compound undergoes a polymorphic change at a temperature of 617°.

The m. p. found for the fluoberyllate Cs_2BeF_4 was 793°. This compound undergoes a polymorphic change at 404°.

The compound $CsBeF_3$ has a congruent melting point at 475° and undergoes two polymorphic changes:

$$\text{liquid} \overset{475^\circ}{\rightleftarrows} \alpha \overset{380^\circ}{\rightleftarrows} \beta \overset{140^\circ}{\rightleftarrows} \gamma.$$

The eutectic Cs_2BeF_4 + $CsBeF_3$ lies at 449° and 48% BeF_2.

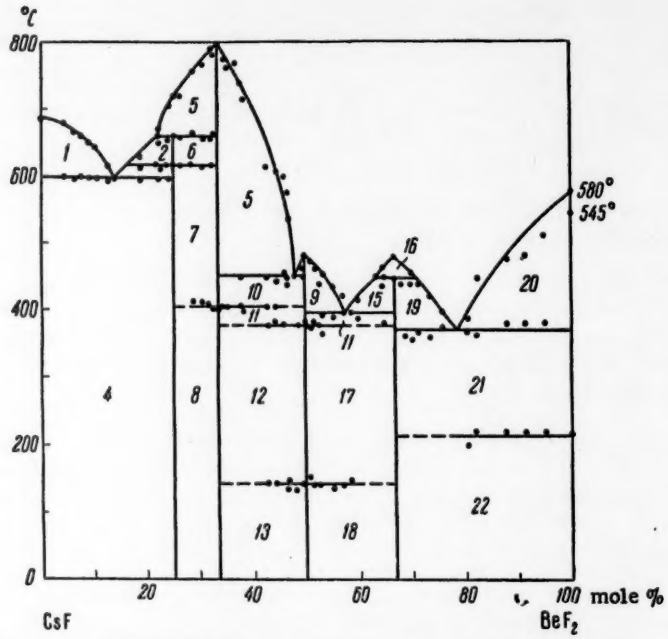

Fig. 1. Multiple phase system $CsF - BeF_2$: *1* — CsF + liq. *2* — α-Cs_3BeF_5 + liq. *3* — β-Cs_3BeF_5 + liq. *4* — CsF + β-Cs_3BeF_5, *5* — α-Cs_2BeF_4 + liq. *6* — α-Cs_3BeF_5 + α-Cs_2BeF_4, *7* — β-Cs_3BeF_5 + + α-Cs_2BeF_4, *8* — β-Cs_3BeF_5 + β-Cs_2BeF_4, *9* — α-$CsBeF_3$ + liq. *10* — α-Cs_2BeF_4 + α-$CsBeF_3$, *11* — β-Cs_2BeF_4 + α-$CsBeF_3$, *12* — β-Cs_2BeF_4 + β—$CsBeF_3$, *13* — β-Cs_2BeF_4 + γ-$CsBeF_3$, *14* — α-$CsBeF_3$ + + β-$CsBe_2F_5$, *15* — β-$CsBe_2F_5$ + liq. *16* — α-$CsBe_2F_5$ + liq. *17* — β-$CsBeF_3$ + β-$CsBe_2F_5$, *18* — γ-$CsBeF_3$ + β-$CsBe_2F_5$, *19* — β-$CsBe_2F_5$ + + liq. *20* — Q_B-BeF_2 + liq. *21* — β-$CsBe_2F_5$ + Q_B-BeF_2, *22* — β-$CsBe_2F_5$ + Q_B-BeF_2

The compound $CsBe_2F_5$ undergoes a polymorphic change at 450°, has a congruent melting point at 480° and forms eutectics with $CsBeF_3$ (393° and 58.4% BeF_2) and with BeF_2 (367° and 77.5% BeF_2).

There is a very striking similarity in the composition diagrams for the systems $CsF-BeF_2$ and $CsF-ZnF_2$ [14]. The existence of cesium fluoberyllates as individual compounds was confirmed by the x-ray phase analysis. In the high-temperature x-ray photography of beryllium fluoride it was found that the quartz-like beryllium fluoride exists up to 580° and then melts. The form similar to crystobalite was found only up to 535°, slowly undergoing conversion to the quartz-like form (detectable from 150°). It is still not clear, however, whether the disappearance of the lines due to the crystobalite-like form of BeF_2 above this temperature is caused by its melting. The high-temperature x-ray analysis also confirmed the polymorphic changes undergone by the compounds $CsBe_2F_5$ and $CsBeF_3$ and showed the absence of polymorphism in cesium fluoride up to 400°. The $\alpha \rightarrow \beta$ conversion for Cs_2BeF_4 was not confirmed, since it was not possible to obtain satisfactory photographs for this compound using the high-temperature camera. The temperature of the $\alpha \rightarrow \beta$ conversion for Cs_2BeF_5 lies above the temperatures at which the nonsilicate capillaries are stable.

The values of the axial lattice parameters for the compounds Cs_2BeF_4 and $CsBeF_3$ were determined from the powder diagrams, the lattices being rhombic. For Cs_2BeF_4 the axial cell parameters are equal to: a = 10.79 A; b = 6.21 A; c = 7.99 A. The density determined using a pyknometer was found to be d_{20} = 4.23, from which $z = 3.91 \approx 4$ and $d_{x\text{-ray}}$ = 4.35. The x-ray diagrams for an oscillating single crystal showed the primitivity of the cell. It is interesting that according to the axial ratio, Cs_2BeF_4 is a better crystallochemical analog of Ba_2SiO_4 then Rb_2BeF_4 [11], in spite of the difference in radii.

The following cell parameters were found for $CsBeF_3$: a = 7.18 A; b = 4.44 A; c = 11.96 A. Density determined by pyknometer d_{20} = 3.43; $d_{x\text{-ray}}$ = 3.46.

Figure 2 shows the relationship between the temperatures of breakdown of the fluoberyllate crystal lattices (congruent melting, noncongruent melting, decomposition in the solid state) and the radii of the cations. It can be seen from the diagram that compounds of the type $M^I_2BeF_4$ are the most stable. The stability of the compounds $M^I_2BeF_4$ increases from Li to Rb and decreases slightly from rubidium to cesium. For the compounds MBe_2F_5 the decomposition temperature remains practically unchanged from Li to K. The compounds with this composition formed by rubidium and cesium are much more stable and have congruent melting points.

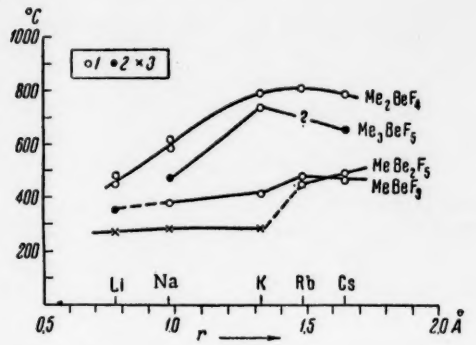

Fig. 2. Relationship between the temperatures of breakdown of fluoberyllate crystal lattices and the radii of the cations. 1) Congruent melting; 2) noncongruent melting; 3) decomposition in the solid state.

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** In Russian.

SYNTHESIS OF AROMATIC HYDROCARBONS

A NEW METHOD FOR THE SYNTHESIS OF HYDROCARBONS OF THE FLUORENE SERIES

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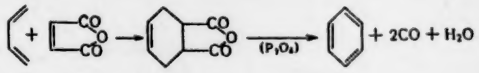
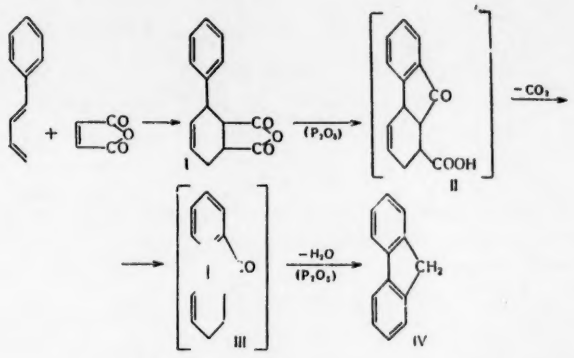
(Presented by Academician A. N. Nesmeianov, September 5, 1957)

As we have shown previously [1-6], the action of phosphorus pentoxide on tetrahydrophthalic anhydrides – products of the addition of dienic hydrocarbons (alkylbutadienes and dicycloalkenyls) to maleic anhydride and its homologs [1-5] and its cyclic analogs [6] – leads to the formation of aromatic hydrocarbons; the reaction proceeds with the liberation of CO and H_2O:

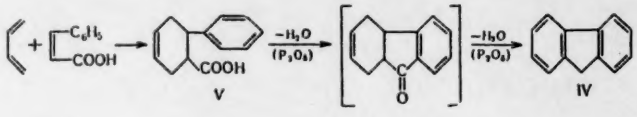


The action of phosphorus pentoxide on phenyltetrahydrophthalic anhydride (I) – the addition product of phenylbutadiene and maleic anhydride – was studied in the present work. It developed that, in this case, the reaction leads to the formation of fluorene (in 21% yield) and not diphenyl, the expected product. The reaction proceeds, apparently, through an intermediate stage of intramolecular acylation of the benzene ring leading to the formation of tetrahydrofluorenonecarboxylic acid (II), and subsequent decarboxylation of the latter to tetrahydrofluorenone (III); the latter is converted to fluorene by the action of phosphorus pentoxide:•

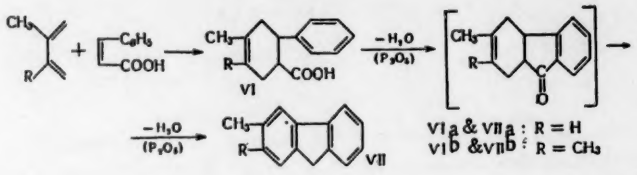


• The possibility of the occurrence of each of the indicated reactions under the influence of phosphorus pentoxide was confirmed by literature data; the literature describes the use of this reagent for intramolecular acylation of a benzene ring [7, 8], for decarboxylation of acids and their derivatives [9], and for the conversion of tetrahydroaromatic ketones (with the carbonyl group in or external to the ring) to aromatic hydrocarbons [10, 11].

Further, we modified and simplified this reaction, using as the starting material phenyltetrahydrobenzoic acid – the product of the addition of butadiene to cinnamic acid (V) – in place of phenyltetrahydrophthalic anhydride. On heating this addition product with phosphorus pentoxide, we obtained fluorene in 63% yield:

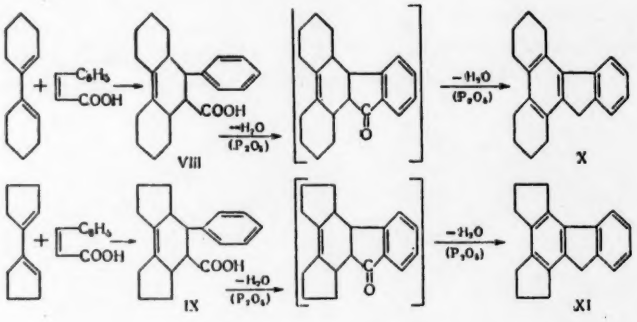


3-Methylfluorene (50% yield) and 2,3-dimethylfluorene (53% yield) were obtained from the products of the addition of cinnamic acid to isoprene and to 2,3-dimethylbutadiene:



That only 3-methylfluorene, m. p. 87.5-88°, and not the isomeric 2-methylfluorene (m. p. 104°), was obtained from the addition product of isoprene and cinnamic acid confirms the structure of this addition product (VIa) as 4-methyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid.

1,2,3,4-Dicyclohexanofluorene (X) and 1,2,3,4-dicyclopentanofluorene (XI) were obtained from the products of the addition of cinnamic acid to dicyclohexenyl (VIII) and to dicyclopentenyl (IX); the yields were 83.5% and 73%:



Thus, the reaction of 2-aryl-1,2,3,6-tetrahydrobenzoic acids (addition products of dienic hydrocarbons and cinnamic acid) with phosphorus pentoxide can be recommended as a new preparative method for the synthesis of hydrocarbons of the fluorene series.

EXPERIMENTAL

Fluorene (IV) from the addition product of 1-phenyl-1,3-butadiene and maleic anhydride. A mixture of 10 g of 1-phenyl-1,3-butadiene (b. p. 75-77°/6 mm; n_D^{20} 1.6088) and 7.5 g of maleic anhydride was carefully heated on a water bath until the reaction started; heating was then stopped, and, after the reaction mixture had cooled, it was again heated for 10 minutes to complete the reaction. The product, 3-phenyl-1,2,3,6-tetrahydrophthalic anhydride (I; 12 g; 70%; m. p. 119-119.5° (from petroleum ether); literature data [12] m. p. 120°), was heated with phosphorus pentoxide (3.7 g) in a Wurtz flask. after completion of the vigorous reaction and cessation of the liberation of gas, distillation gave 1.92 g (21%) of fluorene, which was purified by

sublimation under vacuum; m. p. 113.5-114° (from alcohol). A mixture with a known sample of fluorene melted without depression of the melting point.

Found %: C 93.67, 93.75; H 6.31, 6.21. $C_{13}H_{10}$. Calculated %: C 93.97; H 6.03.

Picrate: m. p. 80-81° (from alcohol). Literature data for fluorene: m. p. 116° [13]; m. p. picrate 80-82° [14].

Hydrocarbons of the fluorene series from addition products of dienes and cinnamic acid.

Fluorene. A mixture of cinnamic acid (m. p. 133°; 50 g; 0.33 mole), butadiene (100 ml; 1.4 mole), absolute benzene (50 ml), and hydroquinone (0.2 g) was heated in an autoclave at 140° for 25 hours. The crystallized reaction mixture, after standing for a day (in the cold), was agitated with a solution of soda; the soda solution was acidified, and the reaction product was extracted with ether; after distillation of the ether, the mixture was heated under vacuum at 140° for partial removal of the cinnamic acid (by sublimation); the m. p. of the residue (20 g) was 79-80°. However, the resulting product V (2-phenyl-1,2,3,6-tetrahydrobenzoic acid) still contained a significant amount of unreacted cinnamic acid (as much as 40%), as judged by melting point (literature value [15], m. p. 101°) and the analytical data.

Found %: C 75.43, 75.56; H 6.66, 6.68. $C_{13}H_{14}O_2$ (addition product). Calculated %: C 77.22; H 6.93. $C_9H_8O_2$ (cinnamic acid). Calculated %: C 72.96; H 5.44.

Since cinnamic acid does not interfere with the reaction of the addition product with P_2O_5 (a special experiment showed that cinnamic acid is converted completely to tar when heated with phosphorus pentoxide), the addition product, without further purification, was heated with phosphorus pentoxide (17 g) until foaming ceased (not above 300°); the fluorene was distilled from the reaction mixture under vacuum (6.2 g; 63% yield); m. p. 115° (after sublimation at 2 mm and recrystallization from alcohol); a mixture with a known sample of fluorene melted without depression of the melting point. M. p. of the picrate was 79-80°. 9-Benzalfluorene (condensation product of fluorene with benzaldehyde [16]) had a m. p. of 75-75.5° (from alcohol); picrate m. p. 113-114° (from alcohol). Literature data [16]: m. p. 76°; picrate m. p. 115°

3-Methylfluorene (VIIa). The reaction between isoprene (17 g; 0.25 mole) and cinnamic acid (14.8 g; 0.1 mole) was carried out in an autoclave in solution in absolute benzene (20 ml) and in the presence of hydroquinone (0.2 g) for 16 hours at 175-180°. After successive treatments of the reaction mixture with soda and with acid, 15 g (70%) of 4-methyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid (VIa) was isolated; m. p. 125.5-126° (from petroleum ether). The literature gives an m. p. of 126° [17]. This addition product was heated with phosphorus pentoxide (9.9 g) until foaming ceased; the reaction product was distilled from the reaction mixture at 190-200°/10 mm. 6.3 g (50%) of 3-methylfluorene was obtained, and this, after washing with alkali and with water, drying, distillation under vacuum, and recrystallization from alcohol, melted at 87.5-88°. The literature [18] gives an m. p. of 88° (2-methylfluorene melts at 104° [19]).

2,3-Dimethylfluorene (VIIb). The addition product of 2,3-dimethylbutadiene (68 g of diene; 0.83 mole) and cinnamic acid (86 g; 0.58 mole) was prepared by the method described for the isoprene addition product, except that xylene (150 ml) was used as the solvent. The reaction mixture was cooled, and the addition product (75 g), m. p. 156-157°, precipitated. Another 10 g of product was isolated (by successive treatments with a 5% solution of potassium hydroxide and with hydrochloric acid) from the residue remaining after distillation of the xylene. The product, 4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydrobenzoic acid (VIb; 55% yield), melted at 159-160° (from acetic acid). The literature [20] gives a m. p. 159-160°. On heating this addition product (15 g) with phosphorus pentoxide (9 g) and subsequent vacuum distillation of the resulting hydrocarbon, 6.9 g (53%) of 2,3-dimethylfluorene was obtained; m. p. 123.5-124.5° (from alcohol). The literature [21] gives an m. p. of 123-124°. The melting point of the picrate (not described in the literature) was 106° (from alcohol).

Found %: N 10.05, 10.13. $C_{21}H_{17}O_7N_3$. Calculated %: N 9.95.

1,2,3,4-Dicyclohexanofluorene (X). The addition product of 1,1'-dicyclohexenyl and cinnamic acid [22] (2-phenyl-3,4,5,6-dicyclohexano-1,2,3,6-tetrahydrobenzoic acid; 7.5 g; m. p. 221.5-222°; literature data [22], m. p. 221°) was heated with phosphorus pentoxide (3.4 g); the reaction product was vacuum distilled at

210-220°/2 mm. The resulting 1,2,3,4-dicyclohexanofluorene (5.5 g; 83.5%) had a m. p. of 129-129.5° (from petroleum ether); the compound is not described in the literature.

Found %: C 92.10, 91.80; H 8.23, 8.31. $C_{21}H_{22}$. Calculated %: C 91.98; H 8.02.

Dicyclohexanofluorene (3 g) was converted to dibenzofluorene by heating with selenium (3.4 g) for 7 hours at 340° (until the liberation of hydrogen selenide completely ceased). Extraction of the reaction mixture with boiling butyl alcohol gave 2.2 g (76%) of 1,2,3,4-dibenzofluorene, m. p. 159-159.5° (from butyl alcohol); the m. p. of the picrate was 153-154° (from butyl alcohol). The literature [23] gives an m. p. of 158-159° for the hydrocarbon and an m. p. of 153-155° for the picrate.

1,2,3,4-dicyclopentanofluorene (XI). The addition product of 1,1'-dicyclopentenyl (16 g) and cinnamic acid (14.6 g) was prepared by the method described for dicyclohexenyl [22] with the exception that the temperature of the reaction mixture was maintained at 160°. At the completion of the reaction, the addition product was extracted with boiling petroleum ether. The yield of addition product – 2-phenyl-3,4,5,6-dicyclopentano-1,2,3,6-tetrahydrobenzoic acid (IX) (not described in the literature) – was 53% (15 g); m. p. 144-145°.

Found %: C 80.87, 81.06; H 7.97, 8.05. $C_{19}H_{22}O_2$. Calculated %: C 80.85; H 7.80.

Reaction of 5 g of this addition product with 2.5 g of phosphorus pentoxide gave 3 g (73%) of dicyclopentanofuran, m. p. 135-136° (from alcohol). The compound is not described in the literature.

Found %: C 92.34, 92.64; H 7.43, 7.32. $C_{19}H_{18}$. Calculated %: C 92.67; H 7.33.

The m. p. of the picrate was 176-176.5° (from acetone).

Found %: N 8.50, 8.43. $C_{25}H_{21}O_7N_3$. Calculated %: N 8.83.

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STEREOISOMERIC 1-METHYL-2-ALKYLCYCLOHEXANES

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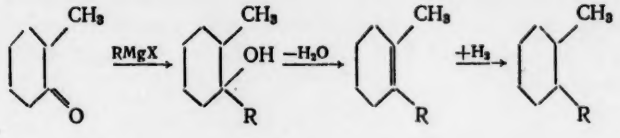
Up to the present, there has been little information in the literature on the stereoisomeric dialkylcyclohexanes. Even in the comparatively more studied series of cis- and trans-1,4-derivatives, there are, at present, reliable data on physical properties for only five pairs of stereoisomers [1-5]: 1,4-dimethyl-, 1-methyl-4-ethyl-, 1-methyl-4-isopropyl-, 1-methyl-4-tert-butyl-, and 1,4-diisopropylcyclohexanes. In the series of 1,2- and 1,3-derivatives, there have been reliable separations only of 1,2- and 1,3-dimethylcyclohexanes [1], 1-methyl-2-ethylcyclohexanes [6], and 1-methyl-3-tert-butylcyclohexanes [4]. Therefore, a study of this class of compounds is extremely interesting, although it presents great experimental difficulties.

Considering the comparatively small amount of related data, we encountered some surprises. Thus, it appears that the cis-form of 1,4-diisopropylcyclohexane boils lower than the trans-isomer [5], although, according to the rule of Auwers-Skita, it should boil higher. The reason for this peculiar inversion of the boiling point remains obscure, and merits further study. In particular, it was of interest to determine whether there would be encountered any similar exceptions in other series of dialkylcyclanes, for example, among the 1,2-dialkylcyclohexanes. With this aim, we decided to synthesize several 1-methyl-2-n-alkylcyclohexanes, and to separate them into their stereoisomers. The syntheses were carried out according to the single scheme:



where, R is n-propyl, n-hexyl, and n-heptyl. The stereoisomers were separated by vacuum rectification in columns having an effectiveness of 100 theoretical plates; the distillations were carried out continuously over the course of several days. Judging from the distillation data, all of the stereoisomers were obtained in a pure form. It developed that the constants of all of the hydrocarbons prepared in the present work were in agreement with the rule of Auwers-Skita. The search for exceptions to this rule continues.

1-Methyl-2-n-hexyl- and 1-methyl-2-n-heptylcyclohexane have not been mentioned in the literature, and 1-methyl-2-n-propylcyclohexane has been previously prepared only as a mixture of the stereoisomers [7], which were not further separated by the authors of that paper.

EXPERIMENTAL

Distillation of the initial, intermediate, and final products was carried out in two glass-packed columns (Nos. 1 and 2) equivalent, respectively, to 20 and 60 theoretical plates and in three columns packed with copper packing and equivalent to 100 theoretical plates, these latter columns were completely equivalent, and all were designated as No. 3.

2-Methyl-1-cyclohexanone of various origins was carefully purified by vacuum distillation in Column No. 3, 15-20 ml fractions being collected. The freezing point curve was determined for each of these fractions,

and only fractions with a freezing point not lower than −13.2° were taken for further work. The unsatisfactorily pure samples were redistilled. The 911 g of ketone obtained by this route had the constants: f. p. −13.2°, n_D^{20} 1.4488, d_4^{20} 0.9251. The purest of these ketone fractions had the constants: b. p. 70.5°/31.5 mm, f. p. − 12.7° (see Fig. 1); the remaining constants did not differ from those given above. Judging from the freezing point curve and the cryoscopic constant (0.0165 mole/degree), the degree of purity of the major portion of ketone was 99.2%, and that of the purest fraction was not less than 99.9%. The most reliable literature data [8] are apparently for a less pure preparation: b. p. 165.08°/760 mm, f. p. −14°, d_4^{20} 0.9250.

The n-propyl chloride (commercial)was distilled in Column No. 2. The fraction collected (440 g) had the properties: b. p. 46.6°/ 760 mm, n_D^{20} 1.3882, d_4^{20} 0.8920. According to the literature [8]: b. p. 46.6°/760 mm, n_D^{20} 1.3888, d_4^{20} 0.8924.

The n-hexyl bromide was prepared from commercial n-hexyl alcohol, which was first distilled in Column No. 1, and which had the constants: b. p. 157.4°/760 mm, n_D^{20} 1.4780, d_4^{20} 0.8188. The literature values are [9]: b. p. 157.4°/760 mm, n_D^{20} 1.4779, d_4^{20} 0.8189. The n-hexyl bromide (394 g) was prepared by the action of a mixture of hydrobromic and sulfuric acids [10] on the alcohol; after distillation under vacuum, the n-hexyl bromide had the following constants: b. p. 55.5°/25 mm, n_D^{20} 1.4476, d_4^{20} 1.1705.

The literature values are [9]: b. p. 156.0°/760 mm, n_D^{20} 1.4478, d_4^{20} 1.1705.

The n-heptyl bromide was prepared from n-heptyl alcohol, which was first distilled under vacuum in Column No. 1; the alcohol had the following constants: b. p. 82.4°/16.5 mm, d_D^{20} 1.4242, d_4^{20} 0.8219. The literature values are [11]: b. p. 176.8°/760 mm, n_D^{20} 1.4242, d_4^{20} 0.8219. The n-heptyl bromide was prepared in the same manner as the n-hexyl bromide. Distillation under vacuum gave 495 g of n-heptyl bromide having the following constants: b.p. 76.0°/23 mm, n_D^{20} 1.4499, d_4^{20} 1.1336. The literature values are [11]: b. p. 180°/ 760 mm, d_4^{20} 1.1335.

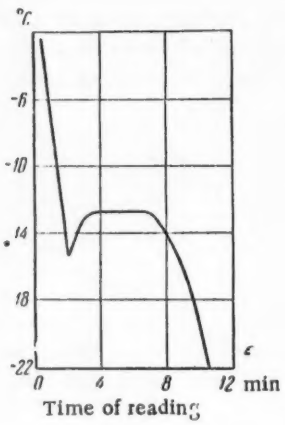


Fig. 1. Freezing point curve of 2-methyl-1-cyclohexanol.

The 2-methyl-1-n-alkyl-1-cyclohexanols were prepared by Grignard synthesis. A large excess of Grignard reagent was used in all cases in order to guarantee complete use of the ketone, which, in view of its considerably difficult preparation in a very pure state, was relatively more valuable than the alkyl halide. All data on yields and constants of the carbinols, which were apparently mixtures of the cis- and trans-forms, are presented in Table 1.

The 1-methyl-2-n-alkylcyclohexenes were prepared by dehydration of the corresponding carbinols in the presence of aqueous oxalic acid (methylethylcyclohexene) or of 2-3 drops of concentrated sulfuric acid; these preparations were mixtures of isomers with the double bond in different positions. Information on the yields and constants is presented in Table 2.

The 1-methyl-2-n-alkylcyclohexanes were prepared, in yields of 88.9-96.5%, by hydrogenation of the corresponding cycloalkenes over platinized carbon (20% Pt) at 150°; the hydrogenation was carried out in a catalyst furnace; the product was chromatographed over silica gel to remove the residual unsaturates. 169.8 g of 1-methyl-2-n-propylcyclohexane, 81.4 g of 1-methyl-2—n-hexylcyclohexane, and 100.7 g of 1-methyl-2-n-heptylcyclohexane were used in the separations of the stereoisomers. The separations were carried out under vacuum in Column No. 3. Cuts were made in regions of temperature rise at a reflux ratio of 200-220; cuts made on plateaus were at the lower reflux ratio of 120-150. During the course of the distillation, small fractions of distillate (from 2 to 15 ml and, only in rare cases, in greater or smaller amounts) were collected, and the index of refraction and density were determined for each fraction. When several successive fractions of distillate had identical constants, the distillate was considered to be the individual stereoisomer. The progression of the constants of the fractions obtained during the distillations is shown in Fig. 2. The properties of the stereoisomers isolated are presented in Table 3.

TABLE 1

Yields and Properties of 2-Methyl-1-alkyl-1-cyclohexanols

R	Used in a single synthesis, moles		Yield, %, of theoretical calc. on ketone	Total obtained in all syntheses g	B. p., °C/mm Hg	n_D^{20}	d_4^{20}
	ketone	alkyl halide					
n-Propyl *	2.27	2.70	84.1	294.4	87–88/13	1.4651	0.9120
n-Hexyl **	1.34	1.70	77.0	256.2	102.0/2.8	1.4655	0.8902
n-Heptyl **	1.20	1.40	69.2	250.9	106.0/2.2	1.4660	0.8916

* According to Signaigo and Cramer [7]: b. p. 65-67°/2 mm, n_D^{20} 1.4653, d_{20}^{20} 0.913.

** Not described in the literature.

TABLE 2

Yields and Properties of 1-Methyl-2-n-alkylcyclohexenes

R	Yields of cyclohexenes, % of theoretical	Cycloalkenes obtained, g	B. p., °C/mm Hg	n_D^{20}	d_4^{20}
n-Propyl *	82.7	193.6	169.0–172.0/745	1.4612	0.8273
n-Hexyl **	88.3	200.5	78–80/2.5	1.4640	0.8312
n-Heptyl **	94.7	130.0	78–80/1.8	1.4655	0.8326

* Signaigo and Cramer [7] give the following constants for 1-methyl-2-n-propyl-1-cyclohexene: b. p. 177.3-177.5°/760 mm, n_D^{20} 1.4627, d_{20}^{20} 0.832.

** Not described in the literature.

TABLE 3

Properties of the Stereoisomeric 1-Methyl-2-n-alkylcyclohexanes

Hydrocarbon		B. p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.
1-Methyl-2-n-propylcyclohexane	trans	66.8/20.5	1.4408	0.7997	46.18	46.30
	cis	69.9/20.5	1.4460	0.8127		46.02
1-Methyl-2-n-hexylcyclohexane	trans	111.2/13.8	1.4490	0.8116	60.26	60.26
	cis	114.0/14.0	1.4527	0.8208		60.06
1-Methyl-2-n-heptylcyclohexane	trans	126.1/13.8	1.4503	0.8143	64.65	64.83
	cis	127.9/13.8	1.4540	0.8229		64.61

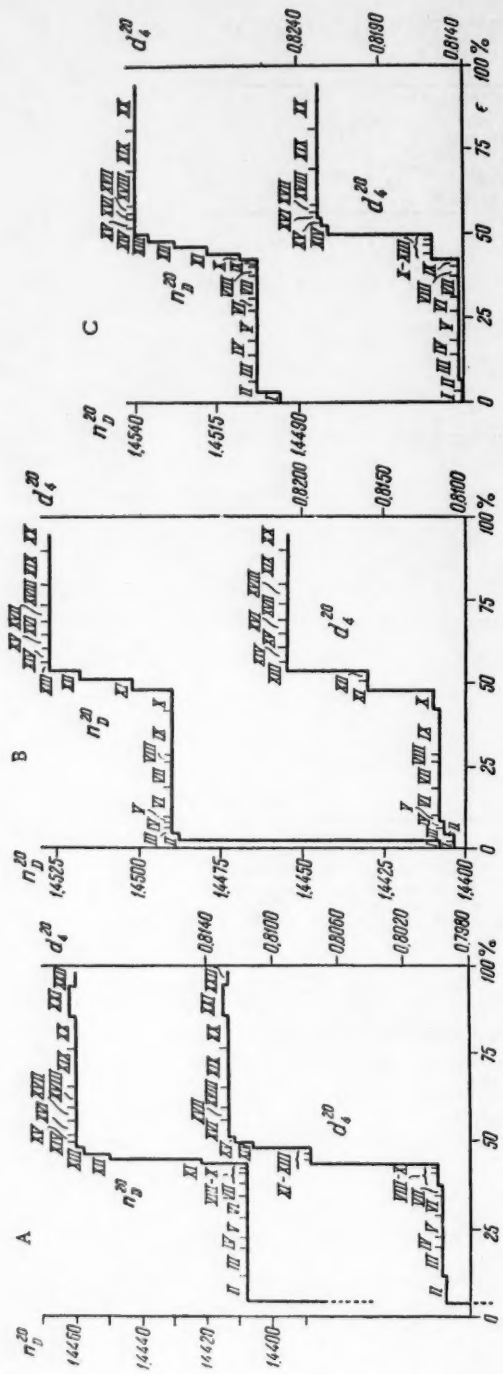


Fig. 2. Indices of refraction and densities of fractions of 1-methyl-2-n-propylcyclohexane (A), 1-methyl-2-n-hexylcyclohexane (B) and 1-methyl-2-n-heptylcyclohexane (C).

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THE INTERACTION OF ATOMIC GROUPINGS SEPARATED FROM EACH OTHER THROUGH A SYSTEM OF TWO BENZENE RINGS CONNECTED BY A BRIDGE

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(Presented by Academician B. A. Kazanskii, October 8, 1957)

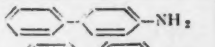
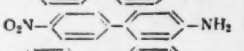
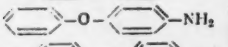
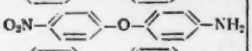
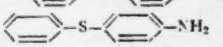
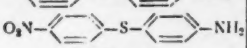
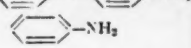
Up to the present, an enormous amount of experimental material has been accumulated in quantitative studies by chemical methods of the mutual influence of atoms or groups of atoms occurring through the simplest of aromatic systems such as the benzene ring. As regards investigations from the point of view of more complex aromatic systems containing several benzene rings, there are only solitary and disconnected publications. Thus, on the basis of a study of the reaction kinetics of the acylation of a series of amino derivatives of biphenyl, we have shown that the interaction of substituents through a system consisting of two directly connected benzene rings, though considerably weakened in comparison with that observed for analogous benzene derivatives, is still rather large [1-3].

It was of interest to determine whether there would appear, and to what extent if it did appear, an interaction between substituents differing sharply in their nature, for example NO_2 and NH_2 groups, occurring on different rings in molecules of compounds in which, in contrast to the previously studied biphenyl derivatives, the benzene rings are not directly connected, but are isolated from each other by a separating link. We were unable to find in the literature any indication that more or less quantitative chemical methods of investigation have been applied to the solution of similar problems; however, a number of such systems have been studied by means their optical properties. From measurements of the absorption spectra of diphenylmethane and its derivatives, N. A. Valiashko and V. F. Lavrushin [4,5] were able to ascertain that the benzene rings of these substances mutually interact through the bridging methylene group. R. S. Tsekhanskii [6] came to a similar conclusion through a study of the nature of the color arising in certain derivatives of diphenylmethane, and Jaffe arrived at the same conclusion through a comparison of the absorption spectra of a number of phenyl derivatives elements of Groups V and VI of the periodic system of elements. A. Kh. Khalilov [8], by measuring the intensity of Raman lines, showed that in diphenylmethane and 1,2-diphenylethane there is considerable interaction of the benzene rings through the aliphatic groups connecting them, while application of this same method to diphenyl ether did not give an unequivocal answer to the question of whether interaction of the benzene rings occurs in this case. In the opinion of V. A. Izmail'skii and A. M. Simonov [9], substitution of N, O, or S atoms for a $-CH{=}CH-$ group in a conjugated chain connecting aromatic radicals leads to a change in the mechanism of transfer of electronic effects along the chain; the indicated atoms are insulators for the conjugation effect, and can act as conductors of only the inductive effect. Koch [10] noted that so-called quasi-conjugation between aromatic rings is observed in diaryl sulfides. A. A. Kharkharov [11] recently commented on the possibility of transfer of a conjugation effect through an NH group. However, Brode [12], also on the basis of spectroscopic data, concluded that group and O, S, CH_2, and NH connecting unsaturated organic radicals are insulators for electronic interaction between the latter. In precisely the same manner, Mangini and Passerini [13] came to the conclusion that the sulfur bridge in aromatic sulfides cannot be considered as a conductor of conjugation.

The present communication is devoted to a study of this question by means of a chemical method. We present here the results of an investigation of the reaction kinetics of the acylation of 4-aminodiphenyl ether, 4-amino-4'-nitrodiphenyl ether, and the corresponding sulfides by p-nitrobenzoyl chloride in benzene solution. The method used for measuring the acylation rate was an improved variant of the method previously

proposed by us [14], and consisted of interrupting the reaction at a specific time by the addition of diethylamine to the reaction mixture, after which the unreacted amine was determined by potentiometric titration with sodium nitrite [15].

TABLE 1

Amine	k, 25°, liter/mole/sec.	k, 50°, liter/mole/sec.	E cal/mole	PZ liter/mole/sec	$\Delta S^{\neq}$, cal/degree/mole	$f_{25°}$
	0.533±0.010	0.11±0.02	5600	$7.1 \cdot 10^8$	−42.8	10.6
	0.0505±0.0011	0.118±0.003	6500	$2.9 \cdot 10^9$	−44.7	
	1.23±0.03	2.60±0.11	5550	$1.49 \cdot 10^8$	−41.5	12.1
	0.102±0.003	0.273±0.006	7500	$3.4 \cdot 10^9$	−39.9	
	0.120±0.006	0.300±0.012	7000	$1.70 \cdot 10^9$	−41.2	23.8
	0.00504±0.00018	0.0178±0.0008	9700	$6.3 \cdot 10^8$	−38.5	
	0.580±0.018	—	—	—	—	

The second order rate constants (k), the energy (E) and entropy (ΔS) of activation, and the frequency factor (PZ) were calculated as indicated in previous communications [2, 3]. The numerical results for each of the reactions investigated are collected in Table 1. Some data from previously studied reactions are presented in the table.

From Table 1, it is seen that, in contrast to phenyl groups which are very weak electron acceptors [1, 2], the C_6H_5O- group displayed a rather appreciable electron donor effect, since, on going from aniline to 4-aminodiphenyl ether, the rate constant increased by more than two-fold. On the contrary, the similar C_6H_5S- group had a clearly expressed electron accepting tendency, since its introduction into the para position of the aniline molecule led to a decrease in the acylation rate by almost a factor of five.

In comparing experimental data characterizing any molecular system from the point of view of its conductance of the mutual influence of substituents, it is convenient to use the ratio of the rate constants for the unsubstituted and the substituted compounds; this ratio reveals how the reaction rate is changed by the influence of a given substituent acting through such a system on the reactive group (for example, in the present case, this characteristic is the ratio of the rate constant for the acylation of the amine without an NO_2 group and that of the amine containing this group in the 4'-position). We call this ratio of constants the factor for the transfer of electronic interaction of substituents, and we denote it by the letter f.

In comparing the diphenyl ether and diphenyl sulfide molecular systems with the biphenyl system, it would be expected that the presence in the first two systems of O and S atoms separating the benzene rings would dictate a considerably weaker interaction between the NO_2 and NH_2 groups than was observed in the case of the biphenyl system where the aromatic rings are directly joined. However, a very unexpected result was obtained; from a comparison of the values of the factor $f_{25°}$, it follows that, on going from the biphenyl system to the diphenyl ether system and the corresponding sulfide system, the interaction of these substituents not only did not decrease, but, on the contrary, even increased slightly in the case of the oxygen-containing compound and became appreciably stronger in the molecule of the diphenyl sulfide derivative. Thus, O and S atoms spatially separating two benzene rings are not insulators of the transfer of electronic effects between these rings. At the present time, in view of the still small amount of experimental material from the study of similar systems by chemical methods, it is not easy to explain this fact, but, most probably, not only do the peculiarities of the spatial structures of these compounds have an essential import (which we will not consider in the present communication), but so also does the presence at the O and S atoms in these compounds of unshared p electrons, which participate in the conjugation with the aromatic rings (p, π-conjugation, according to the definition of A. N. Nesmianov and M. I. Kabachnik [16]). But whatever may be the cause of the peculiar behavior of the amino derivatives studied by us, it remains indisputable that the effect of the removal of one of these substituents from the other, both in the diphenyl ether derivative and in its thio analog,

is overshadowed by some new factor which contributes to the transfer of the interaction of these substituents through the system of two benzene rings joined by a bridging O or S atom.

It should be noted that optical methods of investigation, which have been widely used for studies of the mutual influence of atoms in systems similar to those considered here, frequently lead, as already indicated above, to conflicting results, and do not always expose the same side of this interesting problem as do chemical methods. By a visual comparison of the intensely colored, orange 4-amino-4'-nitrobiphenyl with the light yellow 4-amino-4'-nitrodiphenyl ether and corresponding sulfide, it is readily concluded that the interaction of the NO_2 and NH_2 groups is enormously stronger in the biphenyl derivative, and this has been actually confirmed by spectroscopic investigations of such compounds [13, 17, 18]. However, there is no basis to attribute the contradiction noted in results from studies by chemical and optical methods of the mutual influence of substituents in the present systems to any experimental imperfections of either method. However, the indicated contradiction is merely apparent. The fact is that each of these methods by itself does not permit sufficient characterization of all of the many sides of this complex problem, which we call the mutual influence of atoms and atomic groups not directly connected. The case under consideration serves as an example of this, and all of the material presented above is graphic evidence that such questions must be studied in a variegated manner with the application not only of optical and general physical methods, but also of chemical methods, giving preference to kinetic and equilibrium data on the chemical reactions as being the most rigorous and accurate.

Relative to this, as the reactions investigated in this work by means of energy characteristics point out, we are limited to the observation that the indicated reactions, as well as those previously studied [1-3], proceed at very low values of activation entropy and energy.

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PRODUCTION OF AROMATIC HYDROCARBONS BY CATALYTIC PROCESSING OF THERMALLY CRACKED KEROSENE IN THE PRESENCE OF LIGHT OIL FROM THE CRACKING OF A PETROLEUM STOCK

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(Presented by Academician A. V. Topchiev, October 28, 1957)

In our investigations [1-5], it has been shown that during catalytic processing of various petroleum distillates in the presence of benzene and toluene over silica-alumina, deep conversion of the hydrocarbons of the original distillate to aromatic hydrocarbons occurs, and that a medium of the aromatic hydrocarbons mentioned favors the course of this reaction.

In the development of the cited work, a study of the process of catalytic aromatization of petroleum distillates in the presence of light oil from the cracking of a petroelum stock is of important practical interest. Such a process, in addition to very considerable stabilization of the light oil, provides for the production of an additional amount of low-molecular-weight aromatic hydrocarbons, which have a premium value for the development of processes of petrochemical synthesis.

In the present paper are presented the basic results of an investigation of catalytic aromatization of thermally cracked kerosene in the presence of light oils over synthetic silica-alumina.

The feed stocks used in the investigation were a thermally cracked kerosene and light oils from different cracking processes.

Feed-stock properties are presented in Table 1.

The cracked kerosene boiled in the range 125-310°, and its iodine number was 50.5. 32.2% of the kerosene boiled below 205°. The contents by weight of unsturated, paraffinic, naphthenic, and aromatic hydrocarbons were, respectively, 31.1, 45.6, 16.9, and 6.4%. In other investigations [6, 7], it was shown that the unsaturated hydrocarbons in thermally cracked kerosene are mainly compounds having a cyclic structure.

The light oil from the cracking of an ethane-propane fraction contained practically no paraffinic or naphthenic hydrocarbons. The amount of aromatic and unsaturated compounds in it were, respectively, 73.8 and 26.2%. It was established that the unsturated hydrocarbons in this light oil consisted mainly of styrene, indene, and their homologs. Spectral investigation of a 140-145° fraction separated from the light oil showed the presence of about 90% styrene. The 175-185° fraction differed in having a high content of indene (181°).

The light oil from the cracking of a mixed heavy distillate stock, obtained from the Petroleum Gas Plant in Baku, boiled in the range 42.5-232°. The amount of unsaturated compounds in it generally comprised 31-33%, the aromatics amounted to 60-65%, and the total paraffinic and naphthenic hydrocarbons was 5-9%. The experiments were carried out in a laboratory apparatus with a flow-type reactor, a diagram of which was presented in references [1, 4]. The inspection data and analyses of the feed blends, the catalyzates obtained, and the chief aromatic fractions are presented in Tables 2 and 3.

The weight ratio in the feed stock of cracked kerosene and light oil from ethane-propane cracking was 1 : 2. The contents of benzene, toluene, and xylene fractions were 34.9, 8.5, and 4.1%, respectively. The iodine number of the feed was 65.2; that of the fractions: benzene, 14.7; toluene, 17, xylene, 145.

TABLE 1

Properties of the Thermally Cracked Kerosene and the Light Oils from the Cracking of Petroleum Stocks

	Thermally cracked kerosene		Light oil from the cracking of			
			ethane-propane fraction		heavy distillate stock	
	wt. % distilled	n_D^{20}	wt. % distilled	n_D^{20}	wt. % distilled	n_D^{20}
Fraction composition						
I. b. p. °C	125.0		40.0		42.5	
to 50°	–	–	0.58	1.4675	0.65	1.4355
50-76	–	–	1.57	1.4845	2.58	1.4372
76-78	–	–	0.80	1.4942	0.90	1.4762
78-83	–	–	53.82	1.4999	17.80	1.4870
83-88	–	–	0.50	1.4959	0.90	1.4800
88-95	–	–	0.30	1.4951	0.95	1.4770
95-103	–	–	0.45	1.4950	1.00	1.4750
103-108	–	–	0.40	1.4930	0.93	1.4762
108-113	–	–	15.88	1.4962	30.20	1.4890
113-118	–	–	0.50	1.4941	1.05	1.4760
118-125	–	–	0.43	1.4945	1.15	1.4740
125-132	4.07	1.4175	0.90	1.4992	2.00	1.4732
132-136	0.52	1.4262	0.52	1.5030	1.48	1.4740
136-144	1.60	1.4283	6.38	1.5260	17.48	1.4890
144-149	0.95	1.4316	0.70	1.5240	0.62	1.4925
149-160	3.18	1.4345	1.00	1.5290	2.30	1.4929
160-165	1.00	1.4382	1.81	1.5310	2.95	1.4952
165-175	3.67	1.4400	1.30	1.5420	1.45	1.5030
175-180	2.70	1.4435	1.05	1.5540	3.01	1.5100
180-185	2.85	1.4453	1.50	1.5541	0.85	1.5170
185-K. O.	11.70	1.4493	5.01	1.5546	5.05	1.5472
E. p. °C	205.0		200.0		232.3	
Total distilled, %	32.24		95.4		95.3	
Residue %	66.93		4.1		4.1	
Loss, %	0.83		0.5		0.6	
n_D^{20}	1.4560		1.5102		1.4915	
d_4^{20}	0.8120		0.8888		0.8592	
Sulfonatable, %	35.6		100.0		95.4	
Molecular weight	157		94.0		118.2	
Iodine number						
Group chemical composition, wt. %	50.5		70.5		66.9	
Paraffins	45.6		–		4.0-	
Naphthenes	16.9		–			
Unsaturates	31.1		26.2		31.2	
Aromatics:						
Benzene	–		51.5		17.4	
Toluene	–		15.0		29.0	
C_8	–		2.5		13.0	
C_9 and higher	6.4		4.8		4.4	

TABLE 2

Properties of the Products of the Catalytic Processing of Mixtures of Thermally Cracked Kerosene and Light Oils from Petroleum Cracking. Temperature, 525°C; pressure, 15 atm.; space rate, 0.5 liter/liter/hour, cycle length, 30 minutes

	Feed: cracked kerosene and light oil from gas cracking (wt. ratio, 1:2)		Catalyzate from experiment No. 75		Feed: cracked kerosene and light oil from the cracking of a solar fraction (wt. ratio, 1:2)		Catalyzate from experiment No. 81	
	wt. % distilled	n_D^{20}	wt. % distilled	n_D^{20}	wt. % distilled	n_D^{20}	wt. % distilled	n_D^{20}
Fraction composition	40.0		36.0		42.0		36.1	
I. b. p., °C	0.13	–	3.26	1.3761	0.30	1.3711	0.63	1.3920
to 50°C	0.53	1.4520	1.00	1.4416	1.96	1.4733	1.93	1.4185
50-76	0.50	1.4860	0.60	1.4800	1.20	1.4825	0.50	1.4675
76-78	34.90	1.4990	41.50	1.4965	10.80	1.4894	17.30	1.4840
78-83	0.48	1.4960	0.20	1.4913	0.98	1.4760	0.28	1.4710
83-88	0.78	1.4942	0.35	1.4880	0.78	1.4835	0.30	1.4725
88-95	0.48	1.4930	0.28	1.4862	1.18	1.4833	0.48	1.4720
95-103	0.62	1.4938	0.45	1.4863	1.30	1.4832	0.45	1.4780
103-108	8.48	1.4956	15.10	1.4913	19.11	1.4852	24.43	1.4915
108-113	1.00	1.4941	0.48	1.4870	1.58	1.4778	0.60	1.4840
113-118	1.33	1.4942	0.50	1.4870	1.13	1.4768	0.33	1.4780
118-125	0.90	1.4980	0.53	1.4871	1.19	1.4770	0.40	1.4810
125-132	1.03	1.4990	0.38	1.4872	0.65	1.4780	0.40	1.4875
132-136	4.13	1.5110	9.20	1.4900	10.23	1.4866	17.83	1.4903
136-144	0.53	1.4995	0.43	1.4858	1.53	1.4812	0.33	1.4881
144-149	3.10	1.4873	3.25	1.4833	3.57	1.4770	5.00	1.4860
149-160	1.10	1.4830	2.60	1.4800	4.47	1.4760	2.30	1.4855
160-165	2.00	1.4815	1.21	1.4795	2.23	1.4766	3.73	1.4835
165-175	1.33	1.4800	0.85	1.4790	1.67	1.4741	1.83	1.4810
175-180	1.65	1.4810	1.15	1.4800	1.20	1.4718	0.75	1.4800
180-185	10.60	1.4880	4.53	1.4900	2.45	1.4722	6.70	1.4800
185- K. O.								
End point, °C	205.0		204.5		195.0		205.0	
Total distilled, wt. %	75.6		87.87		69.51		87.5	
Residue %	22.4		11.70		29.70		10.6	
Loss, %	2.0		0.43		0.79		1.9	
n_D^{20}	1.4919		1.4852		1.4802		1.4890	
d_4^{20}	0.8603		0.8514		0.8447		0.8398	
Sulfonatable, %	78.0		92.3		76.4		92.0	
Iodine number	65.2		0.22		61.4		0.22	
Material balance, wt. %								
Catalyzate	–		91.0		–		91.4	
Gas	–		3.8		–		3.8	
Coke	–		5.2		–		4.8	
Loss	–				–			

TABLE 3

Properties of the Major Aromatic Fractions

	Fractions of feed: cracked kerosene and light oil from gas cracking (wt. ratio, 1:2)	Fractions of catalyzate, experiment No. 75	Fractions of feed: cracked kerosene and light oil from cracking of solar fraction (wt. ratio, 1:2)	Fractions of catalyzate, experiment No. 81
78-83° fraction				
Yield, % of catalyzate	34.9	41.5	10.8	17.3
n_D^{20}	1.4990	1.4965	1.4894	1.4840
d_4^{20}	0.8668	0.8659	0.8595	0.8511
Sulfonatable, %	100.0	97.0	94.5	90.1
Bromine number	14.7*	0.2	48.7*	0.1
108-113° fraction				
Yield, % of catalyzate	8.48	15.10	19.11	24.43
n_D^{20}	1.4956	1.4913	1.4852	0.4915
d_4^{20}	0.8655	0.8601	0.8532	0.8630
Sulfonatable, %	100.0	96.0	92.5	96.9
Bromine number	16.9*	0.08	18.9*	0.1
136-144° fraction				
Yield, % of catalyzate	4.13	9.2	10.23	17.83
n_D^{20}	1.5110	1.4900	1.4866	1.4903
d_4^{20}	0.8794	0.8601	0.8545	0.8606
Sulfonatable, %	100.0	94.6	94.0	94.9
Bromine number	145.0*	0.08	87.5*	0.16

*Iodine number.

Complete chemical stabilization of the unsaturated hydrocarbons was achieved at a temperature of 525°, a pressure of 15 atm., and a space rate of 0.5 liter/liter/hour with a single pass of the feed over the catalyst. Deep-seated aromatization of the thermally cracked kerosene occurred. The iodine number of the product was 0.2. The catalyzate contained 92.3% sulfonatable material. The amounts of benzene, toluene, and xylene were, respectively, 41.5, 15.1, and 9.2% of the catalyzate. The bromine number of the specific aromatic hydrocarbons vaired from 0.08 to 0.2, and the amount sulfonatable varied from 94 to 97%. The yield of catalyzate was 91%, that of the gas was 3.8%, and that of coke was 4.6%.

The properties of the blend of light oil from the cracking of a heavy distillate stock with thermally cracked kerosene and of the catalyzate obtained by the processing of this blend are presented in Tables 2 and 3.

Under optimum conditions, deep destruction of the kerosene hydrocarbons took place. The amount of fractions boiling above 200° decreased from 30 to 10%, and, inversely, there was an increase in the amount of fractions boiling up to 200°. The iodine number decreased from 61 to 0.2. There was an appreciable increase in the amounts of the benzene, toluene, and xylene fractions.

A spectral investigation of the xylene fractions of the catalyzates showed that the amounts of ortho-, para-, and meta-isomers and of ethylbenzene were, respectively, 22-25, 29-35, 37.5-46, and 2-5.7%.

In Table 4 are presented material balances of characteristic experiments.

The yield of the broad fraction (e. p. 205°) comprised about 80% of the feed mixture. When a mixture of cracked kerosene and the light oil from gas cracking was processed, the yields of benzene, toluene, and

TABLE 4

Process Material Balance

Product	Experiment No. 75		Experiment No. 81	
	fed	obtained	fed	obtained
Thermally cracked kerosene	33.3	–	33.3	–
Light oil from gas cracking	66.7	–	–	–
Light oil from cracking of heavy distillate stock	–	–	66.7	–
Stable fraction (205° e.p.)	–			
Specific fractions:	–	80.0	–	80.2
Benzene (78-83°)	34.9•	37.8	10.8•	15.0
Toluene (108-113°)	8.5•	14.7	19.1•	23.4
Xylene and ethylbenzene (136-144°)	4.1•	9.0	10.2•	16.3
Residue above 205°	22.4	10.6	29.1	9.7
Gas	–	3.8	–	3.8
Coke	–		–	
Loss	–	5.6	–	6.5

• Raw aromatic fractions.

C_8 aromatic hydrocarbons were, respectively, 37.8%, 14.7%, and 9.0%. When a mixture of thermally cracked kerosene and the light oil from the cracking of a heavy distillate stock was processed, the yields of benzene, toluene, and xylenes plus ethylbenzene were, respectively, 15.0%, 23%, and 16.3%, all based on the feed processed.

The gaseous products of the experiments consisted of 86-87% methane and its homologs, 9-10% hydrogen, and 3-3.5% unsaturated hydrocarbons.

The proposed process of aromatization of products of thermal cracking and pyrolysis of petroleum is a good prospect for the development of the production of aromatic hydrocarbons, and its wide-spread use would permit a considerable increase in the resources of benzene, toluene, and xylenes.

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ADDITION REACTIONS OF NITROALKANES TO BENZALACETONE

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The first investigations devoted to a study of the addition of nitroalkanes to α,β-unsaturated ketones were published in 1916. Thus, Kohler [1] discovered that the sodium salt of nitromethane readily enters into reaction with benzalacetophenone with the formation of γ-nitro-β-phenylbutryophenone:

$$C_6H_5CH = CHCOC_6H_5 + CH_2 = NO_2Na \rightarrow C_6H_5 - \underset{\displaystyle CH_2NO_2}{\underset{|}{CH}} - CH_2COC_6H_5.$$

This reaction occurs only in the presence of basic catalysts (sodium methylate, diethylamine, or piperidine). Free nitromethane does not react with benzalacetophenone.

Subsequently, Kohler [2] added nitromethane to benzalacetone in the presence of sodium methylate:

$$C_6H_5 - CH = CHCOCH_3 + CH_3 = NO_2Na \rightarrow C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{CH}} - CH_2COCH_3.$$

In 1947, Klotzel [3] described the addition of nitromethane and 1- and 2-nitropropanes to benzalacetone and other unsaturated ketones, and showed that the synthesis of priorly difficultly attainable substances is feasible by such a route. However, the course of this reaction as it depends on the number and positions of nitro groups in the nitroalkanes was not studied in the cited work. In the present work, the addition of different mono- and polynitroalkanes to benzalacetone was studied in relation to the number of nitro groups and their positions in the molecule.

2-Nitro-3-phenyl-5-hexanone was obtained in low yield by the reaction of nitroethane with benzalacetone in the presence of a catalyst (an alcoholic solution of trimethylphenylammonium ethylate):

$$C_6H_5 - CH = CHCOCH_3 + CH_3CH_2NO_2 \rightarrow C_6H_5\underset{\displaystyle H_3C - CHNO_2}{\underset{|}{CH}} - CH_2COCH_3.$$

1,1-Dinitroethane enters into the reaction considerably more readily, and the reaction proceeds with the formation of 2,2-dinitro-3-phenyl-5-hexanone in high yield:

$$C_6H_5 - CH = CH - COCH_3 + CH_3CH(NO_2)_2 \rightarrow CH_3COCH_2\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\underset{\displaystyle NO_2}{\underset{|}{C}} - CH_3.$$

The considerably more acidic nitroalkane trinitromethane adds to benzalacetone still more actively and in the absence of catalysts; 1,1,1-trinitro-2-phenyl-4-pentanone is formed in high yield (80% of theoretical):

$$C_6H_5CH = CHCOCH_3 + CH(NO_2)_3 \rightarrow C_6H_5\underset{\displaystyle C(NO_2)_3}{\underset{|}{C}}H - CH_2COCH_3.$$

It is interesting to note that dinitromethane readily adds to benzalacetone in the presence of catalysts with the formation of 1,1-dinitro-2-phenyl-4-pentanone, and the reaction does not yield the product of the addition of dinitromethane to two molecules of benzalacetone, which is a product of certain other dinitromethane reactions described in the literature [4].

EXPERIMENTAL

The benzalacetone, prepared from benzaldehyde and acetone [5], had the following constants: b. p. 129-130°/7 mm, m. p. 41.5-42°.

Literature data for benzalacetone: b. p. 128-130°/13 mm, m. p. 37-38° [6] and 41.5° [7].

The addition of the nitroalkanes to benzalacetone was carried out in a four-necked flask fitted with a mechanical stirrer, a dropping funnel, a thermometer, and a reflux condenser.

Addition of nitroethane. To a solution of 7.5 g (0.1 mole) of nitroethane in 25 ml of ethanol was added 0.01 mole of an alcoholic solution of trimethylphenylammonium ethylate, and then, with stirring, was added 14.6 g (0.1 mole) of benzalacetone. The mixture was heated on a boiling water bath for 10-12 hours. The solvent was then distilled, and the residue was distilled under vacuum.

There was obtained: Fraction I, 110-130°/3 mm (4.2 g);
Fraction II, 130-140°/3 mm (2.2 g).

Fraction II was 2-nitro-3-phenyl-5-hexanone, which, after redistillation, had a b. p. of 137°/3 mm.

Found %: C 65.59, 65.79; H 6.96, 6.77; N 6.48, 6.56. $C_{12}H_{15}NO_3$. Calculated %: C 65.10; H 6.79; N 6.34.

Addition of 1,1-dinitroethane. To a solution of 4.7 g (0.06 mole) of 1,1-dinitroethane in 20 ml of ethyl alcohol was added 0.006 mole of trimethylphenylammonium ethylate; 12.3 g of benzalacetone was then added with stirring, following which the mixture was heated on a boiling water bath for 10 hours. White crystals precipitated during cooling of the reaction mixture, and these were filtered. 0.5 g of a material with a m. p. of 102-103° was obtained. After recrystallization from ethyl alcohol, the 2,2-dinitro-3-phenyl-5-hexanone melted at 103°.

Found %: C 54.07, 53.88; H 5.46, 5.51; N 10.31, 10.31. $C_{12}H_{14}O_5N_2$. Calculated %: C 54.2; H 5.26; N 10.5.

The dinitrophenylhydrazone, m. p. 143°, was prepared.

Addition of dinitromethane. 0.01 mole of trimethylphenylammonium ethylate in alcohol was added to a solution of 10.6 g (0.1 mole) of dinitromethane in 30 ml of methanol. 14.6 g of benzalacetone was then added, after which the mixture was heated on a water bath for 2 hours. The reaction mixture was then diluted with water and extracted with ether. The ethereal solution was dried with calcined Na_2SO_4. After distillation of the ether under vacuum, the residue crystallized.

15 g (60% of theoretical) of 1,1-dinitro-2-phenyl-4-pentanone, m. p. 94° after recrystallization from alcohol, was obtained.

Found %: C 52.73, 52; H 4.75; N 11.28. $C_{11}H_{12}O_5N_2$. Calculated %: C 52.48; H 4.77; N 11.10.

Addition of trinitromethane. 14.6 g (0.1 mole) of melted benzalacetone was added dropwise, with stirring, to a solution of 15.1 g (0.1 mole) of trinitromethane in 45 ml of alcohol. The mixture was then heated at 70° on a water bath for 1.5 hours (after 15-20 minutes, crystals began to precipitate from the solution). The reaction mixture was cooled, and the precipitate was filtered and washed with alcohol. There was obtained 23.2 g (80% of theoretical) of 1,1,1-trinitro-2-phenyl-4-pentanone – a white crystalline substance with a m. p. of 91° after recrystallization from alcohol.

Found %: C 43.16; H 3.75; N 14.09. $C_{11}H_{10}N_3O_7$. Calculated %: C 44.30; H 3.70; N 14.10.

The dinitrophenylhydrazone, m. p. 160°, was prepared.

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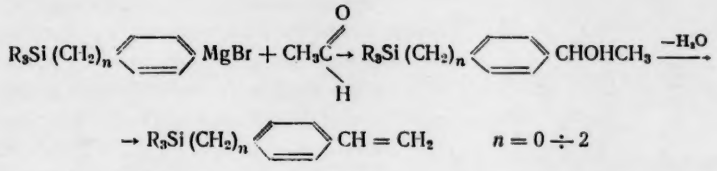
SYNTHESIS OF p-TRIALKYLSILYL- AND p-TRIALKYLSILYLALKYLSTYRENES

Corresponding Member AN SSSR A. D. Petrov, E. A. Chernyshev and N. G. Tolstikova

Up to the present, synthesis routes have been developed for a very large number of unsaturated organosilicon compounds, and the properties of these compounds have been studied [1, 2]. In particular, a very detailed study has been made of the tendency of such compounds to polymerize [3-5]. As regards the synthesis of compounds in which silicon is substituted in styrene rings, only two patents have dealt with this question, and these gave neither a detailed description of the synthesis nor the properties of the compounds obtained [6, 7].

The aim of the present work was to develop routes for the synthesis of silicon-containing styrenes in which the silicon was substituted in the ring in the para-position. The overall scheme of the synthesis of these compounds consisted of a Grignard reaction to obtain the appropriate alcohol, and dehydration of the alcohol to the silicon-containing styrene:



Grignard reactions of p-trimethyl- and p-triethylsilylphenylmagnesium bromides with acetaldehyde and acetone were successfully carried out, and gave the corresponding alcohols in yields of 40-60%. Dehydration under mild conditions by refluxing the alcohols over $KHSO_4$ was not very successful; the secondary alcohols were only partially dehydrated. Therefore, the alcohols were dehydrated over Al_2O_3 at 340-350° and an absolute pressure of 150-160 mm. This method gave satisfactory results, although in this case partial polymerization of the resulting styrene occurred. The styrenes were obtained in yields of 30-50%.

In order to use this scheme for the synthesis of R_3SiCH_2 $CH=CH_2$ and $R_3SiCH_2CH_2$ $CH=CH_2$, it was necessary to develop a method for the preparation of Cl_3SiCH_2 Br and $Cl_3SiCH_2CH_2$ Br. Iakubovich and Motsarev [8] recently reported the bromination of benzyltrichlorosilane with bromide; however, the proof of structure of the compounds obtained could not be considered strictly reliable. We also brominated benzyltrichlorosilane with bromine in the cold and in the presence of Fe. Distillation in a column showed that only one product resulted. β-Phenylethyltrichlorosilane was also brominated under these same conditions, and only a single product was isolated. Both of these compounds were analyzed spectroscopically. It was shown in reference [9] that the type of substitution, ortho, meta, or para, in disubstituted benzene derivatives could be identified by infrared absorption spectra in the 5-6μ region. The spectra of the above-mentioned bromides, preliminarily ethylated, were obtained with an IKS-11 spectrograph with an NaCl prism. The spectra were similar, and contained only two bands (1775 and 1880 cm^{-1}) which are characteristic of the para-isomers, according to the cited work.

TABLE 1

Initial organosilicon bromide	Initial carbonyl compound	Alcohol obtained	Yield, %	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	OH, % calc.	OH, % found
$(CH_3)_3Si$–C$_6$H$_4$–Br	$CH_3C(=O)H$	$(CH_3)_3Si$–C$_6$H$_4$–$CHOHCH_3$	47.1	91—92/2	1.5148	0.9611	8.72	8.45 8.40
$(CH_3)_3Si$–C$_6$H$_4$–Br	CH_3COCH_3	$(CH_3)_3Si$–C$_6$H$_4$–$COHCH_3$–CH_3	46	115—116/8	1.5130	0.9552	8.14	7.88 8.00
$(C_2H_5)_3Si$–C$_6$H$_4$–Br	$CH_3C(=O)H$	$(C_2H_5)_3Si$–C$_6$H$_4$–$CHOHCH_3$	57.6	136—137.5/3	1.5195	0.9624	7.16	6.82 6.94
$(C_2H_5)_3Si$–C$_6$H$_4$–Br	CH_3COCH_3	$(C_2H_5)_3Si$–C$_6$H$_4$–$COHCH_3$–CH_3	34.8	138—138.5/6	1.5213	0.9374	6.77	6.64 6.60
$(C_2H_5)_3SiCH_2$–C$_6$H$_4$–Br	$CH_3C(=O)H$	$(C_2H_5)_3SiCH_2$–C$_6$H$_4$–$CHOHCH_3$	13	137—138.5/4	1.5291	0.9544	6.42	6.14 6.32
$(C_2H_5)_3SiCH_2CH_2$–C$_6$H$_4$–Br	$CH_3C(=O)H$	$(C_2H_5)_3SiCH_2CH_2$–C$_6$H$_4$–$CHOHCH_3$	13	185—187/6.5	1.5172	0.9533	6.09	5.77 5.69

Grignard reactions of $(C_2H_5)_3SiCH_2$–C$_6$H$_4$–Br and $(C_2H_5)_3SiCH_2CH_2$–C$_6$H$_4$–Br with acetic anhydride gave the corresponding alcohols in yields of only 13%. Considerable amounts of benzyltriethylsilane and β-phenylethyltriethylsilane, respectively, formed during the decomposition by water of the unreacted Grignard reagents, were isolated. Dehydration of the first alcohol over Al_2O_3 gave the corresponding styrene in 50% yield. Dehydration of the second alcohol also gave a certain amount of the corresponding styrene, which, however, completely polymerized during distillation over Na. Polymerization of the styrenes obtained was not studied.

The bromination of benzyltrichlorosilane, obtained from benzyl chloride and $SiCl_4$ by Grignard reaction, was carried out in a three-necked flask fitted with a stirrer, a dropping funnel, and a reflux condenser. 580 g (2.59 moles) of benzyltrichlorosilane and 5 g of iron filings were placed in the flask, and, with stirring, 425 g (2.66 moles) of bromine was added over a period of 10 hours. The temperature of the cooling bath was maintained in the range of 10-20°. After the addition of bromine was complete, the mixture was heated for 20 minutes at 70°. Then dry nitrogen was passed through the mixture for 5 hours to remove the HBr. Distillation under vacuum in a column of 30 theoretical plates gave 485 g of p-bromobenzyltrichlorosilane, 61.7% yield, b. p. 135°/12.5 mm, n_D^{20} 1.5600, d_4^{20} 1.6008, MR_D 61.51 (calc. 61.09). β-Phenylethyltrichlorosilane, obtained by the method described in [10], was brominated under the same conditions. From 700 g of β-phenylethyltrichlorosilane was obtained 510.5 g of β-(p-bromophenyl)ethyltrichlorosilane, 55% yield, b. p. 141°/7 mm, n_D^{20} 1.5481, d_4^{20} 1.5390, MR_D 65.75 (calc. 65.71).

Both bromides were ethylated by means of C_2H_5MgBr, yielding p-bromobenzyltriethylsilane (75% yield, b. p. 140.5-141°/5 mm, n_D^{20} 1.5324, d_4^{20} 1.1560, MR_D 76.52, (calc. 76.17) and β-(p-bromophenyl)ethyltriethylsilane (80.5% yield, b. p. 149°/4.5 mm, n_D^{20} 1.5248, d_4^{20} 1.1420, MR_D 80.21, calc. 80.29).

p-α-Hydroxyethylphenyltrimethylsilane was prepared by Grignard reaction; the reaction was carried out in a three-necked flask fitted with a stirrer, a dropping funnel, and a reflux condenser. 80 g (1.8 moles) of acetaldehyde was slowly added to the Grignard reagent, which was prepared from 210 g (0.91 mole) of p-bromophenyltrimethylsilane. The temperature of the reaction mixture was maintained at 5-10° by cooling the bath with ice water. After the aldehyde was was added, the mixture was stirred at room temperature

TABLE 2

Silicon-substituted styrene	Yield, %	B. p. °C/mm Hg	n_D^{20}	d_4^{20}	Calculated %			Found %		
					C	H	Si	C	H	Si
$(CH_3)_3Si$–C$_6$H$_4$–CH=CH$_2$	38.9	101–101.5/20	1.5221	0.8979	75.06	9.09	15.91	74.72 74.62	9.06 9.02	15.72 15.50
$(CH_3)_3Si$–C$_6$H$_4$–C(CH$_3$)=CH$_2$	52.3	110–111/20	1.5188	0.8828	75.79	9.47	14.74	75.49 75.58	9.47 9.42	14.62 14.46
$(C_2H_5)_3Si$–C$_6$H$_4$–CH=CH$_2$	40.4	107–107.5/3	1.5295	0.9203	77.06	10.09	12.85	76.98 76.88	10.02 10.07	12.68 12.77
$(C_2H_5)_3Si$–C$_6$H$_4$–C(CH$_3$)=CH$_2$	32.5	132–133/7.5	1.5218	0.9070	77.58	10.35	12.07	77.52 77.48	10.30 10.30	12.00 12.13
$(C_2H_5)_3SiCH_2$–C$_6$H$_4$–CH=CH$_2$	51.6	126–127/3.5	1.5237	0.9256	77.58	10.35	12.07	77.12 77.24	10.20 10.12	11.93 11.9

for three hours and then for another three hours under reflux. The mixture was then decomposed as usual, and the organic layer was dried over anhydrous Na_2SO_4. Distillation gave 84.3 g of p-α-hydroxyethylphenyltrimethylsilane; the yield was 47.1%. The properties of the alcohol are presented in Table 1. All of the other alcohols were synthesized under the same conditions. The results of the experiments are presented in Table 1.

Dehydration of these alcohols was carried out over calcined Al_2O_3 at 330-340° in an ordinary catalyst furnace. The alcohols were fed at a rate of 0.5 cc/minute. The entire system was maintained under a reduced pressure of 170 mm Hg, which was created by an aspirator. The resulting product was dried over Na_2SO_4, and distilled under vacuum. The properties and yields of the alcohols synthesized are presented in Table 2.

We express our deep appreciation to Iu. P. Egorov, who carried out the spectral analyses of the bromobenzyl- and bromophenylethyltriethylsilanes.

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RADICAL-EXCHANGE REACTIONS IN THE PRESENCE OF $AlCl_3$

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(Presented by Academician V. N. Kondrat'ev, October 23, 1957)

Using organometallic compounds, we have previously investigated radical exchange with the "solvent." In these studies, it was shown that exchange proceeds by both radical and ionic reactions. In reactions of organomercury compounds, the exchange proceeds through free radicals with regeneration of the reacting radical [1]. Organosodium compounds exchange with the "solvent" by a carbanion mechanism [2]. The exchange was more complete in the latter case, and it occurred between radicals such as benzyl, for example, which cannot not exchange as a free radical.

In the present work, we wished to verify the possibility of exchange by a cationic mechanism:

$$R^+ + R^*D \rightleftarrows R^{*+} + RD, \qquad (1)$$

and a deuterium-containing "solvent" and $AlCl_3$, as the catalyst, were used for this purpose.

The use of $AlCl_3$ as a catalyst for hydrogen exchange has been investigated mainly for acid-type reactions [3].

$$\begin{gathered} DX + RH + AlCl_3 \rightleftarrows D^+ + RH + (AlCl_3X)^- \\ D^+ + RH \rightleftarrows H^+ + RD. \end{gathered} \qquad (2)$$

Exchange reactions occurring through carbonium ions have been investigated by means of deuterium in reactions between aliphatic hydrocarbons and H_2SO_4 [4, 5].

We used organic halides and aromatic hydrocarbons for the study of cationic exchange. The compounds selected as the exchanging systems interact in two ways with $AlCl_3$. As is well known, halide compounds yield carbonium ions in the presence of $AlCl_3$ [6, 7]. Exchange proceeds according to Equation (1) in this case. Aromatic hydrocarbons interact with $AlCl_3$ to yield a π-complex in which the aromatic hydrocarbon tends strongly toward protonization [8]. Exchange is then possible by Reaction (2).

As seen from Table 1, in the chlorobenzene–deuteriobenzene and the cyclohexyl chloride–deuteriocyclohexane systems (Experiments Nos. 1-5), exchange in the presence of $AlCl_3$ goes to equilibrium as defined by:

$$RXI + R^*D \overset{AlCl_3}{\rightleftarrows} R^*XI + RD.$$

Exchange proceeds in these systems by Equation (1) through phenyl and cyclohexyl carbonium ions, the formation of which proceeds according to

$$R-\overline{Cl}| + AlCl_3 \rightleftarrows R^+ + (AlCl_4)^-,$$
$$R + R^*D \rightleftarrows (R \rightarrow R^*D) \rightleftarrows RD + R^{*+},$$
$$R^{*+} + (AlCl_4)^- \rightleftarrows R^*\overline{Cl}| + AlCl_3.$$

It is possible that deuterolysis of the deuteriobenzene promoted the hydrogen-exchange reaction in Experiments Nos. 1-4.

$$C_6D_5D + AlCl \rightarrow D^+ + (C_6D_5AlCl_3)^-.$$

However, it follows from the results obtained with the cyclohexyl chloride–deuteriocyclohexane system that this condition is not required.

TABLE 1

Expt. No.	Exchanging components		Temperature, °C	Time, hours	Content of D* in original component II, γ	Content of D* component I after reaction, γ	Exchange %	Error in measurements***, %
	I	II						
1	C_6H_5Cl	C_6D_6	18	72	2000	85	4.2	0.5
2	The same	The same	50	1/2	2740	916	33.4	0.3
3	" "	" "	100	1/3	2740	1270	43.4	0.3
4	" "	" "	100	24	4820	2240	46.5	0.2
5	$C_6H_{11}Cl$	$C_6H_{11}D$	18	21	4152	1900	45.7	2.5
6	$-CH_2C_6H_4Br$	$CH_3OC_6H_3D_2$	18	24	10380	324	3.1	0.2
7	The same	The same	100	3	10380	442	4.2	0.2
8	p-$NO_2C_6H_4Cl$	$NO_2C_6D_5$	18	24	3367	259	7.6	1.8
9	The same	The same	100	3	8600	362	4.2	0.4
10	$C_6H_5CH_3$	C_6D_6	100	3	5050	3565	70.6	1.8
11	To same	The same	100	3	5050	3460	68.6	1.9
12	C_6H_{12}	C_6D_6	18	24	5050	125	2.4	0.8
13	The same	The same	100	3	5050	36	0.7	0.6
14	C_6H_{12}	$C_6H_{11}D$	18	24	4152	100	2.4	2.4
15	The same	The same	100	3	4152	350	8.4	2.4
16	$C_6H_5OC_2H_5$	C_6D_6	100	3	5050	39	0.4	0.3
17	$C_6H_5CH_2OCH_2C_6H_5$	$CH_3C_6D_5$	18	24	8600	89	1.0	0.3
18	The same	The same	100	3	8600	4,0	0.1	0.3

TABLE 2

Expt. No.	Exchanging components		Temperature, °C	Time, hours	Content of C^{14} in original component II, imp./min.	C^{14} found in component I after reaction imp/min	Exchange %	Error in measurements***, %
	I	II						
1	$CH_3C_6H_5$	C_6H_5—1—$6C^{14}$	100	3	1536	176	11.4	0.2
2	The same	The same	100	3	1536	219	14.3	0.2
3	" "	" "	100	3	1536	190	12.4	0.2

* Amount of deuterium present in the ring of the aromatic compound.

** The per cent exchange was calculated taking into account the reaction equilibrium. In Experiments Nos. 16-18, it was calculated for two exchanging groups.

*** The experimental error (in %) was calculated as the ratio of the product of the error in measurement (15 γ) and the dilution to the deuterium content of original component II.

In contrast to these systems, hydrogen exchange between toluene and deuteriobenzene (Table 1, Experiments Nos. 10 and 11) proceeded only according to Equation (2):

$$C_6D_6 + AlCl_3 \rightleftarrows (C_6D_5AlCl_3)^- + D^+,$$
$$C_6H_5CH_3 + AlCl_3 \rightleftarrows (C_6H_4CH_3AlCl_3)^- + H^+.$$

The exchanging fragments are a proton and a deuteron. The exchange process can also be represented as an electrophilic substitution reaction

$$C_6D_6 + H^+ \rightleftarrows (C_6D_6H)^+ \rightleftarrows C_6H_5H + D^+.$$

It is well known that hydrogen transfer from the CH_3 group to the ring and also from one position to another in a toluene molecule does not occur [9, 10].

Since many $AlCl_3$-catalyzed reactions are accompanied by rearrangements (as, for example, Friedel-Crafts reactions), it was necessary to check the exchange between toluene and benzene using two isotopic labels. For this purpose, we selected deuteriotoluene labeled in the ring and radiobenzene 1-6 C^{14}. The experiment showed that, together with hydrogen exchange, there was also an intermolecular migration of the CH_3 group from the toluene to the benzene ring. The rearrangement amounted to about 12.7% after 3 hours at 100°. This was established by the presence of radiocarbon in the toluene, which was isolated as benzoic acid (Table 2, Experiments Nos. 1-3).

The investigation of exchange reactions between deuteriobenzene and cyclohexene and between cyclohexene and deuteriocyclohexane (Table 1, Experiments Nos. 12-15) showed that there is practically no exchange in these systems. To a certain extent, these experiments confirm the correctness of the conclusions formed above. Actually, in the case where one of the components does not form a π-complex with $AlCl_3$ (for example, cyclohexane) or where the formation of the complex is not accompanied by protonization (for example, with cyclohexene), hydrogen exchange does not occur.

The experiments with chloronitrobenzene and with bromoanisole were undertaken to study the effect of substituents of the exchange process. It seemed that electrophilic substituents, which increase the charge on the carbonium ion, should promote the exchange process, while nucleophilic substituents, which decrease this charge, should slow down the exchange rate. However, the experiments showed that, under the above conditions, p-chloronitrobenzene and o-bromoanisol exchanged very little with deuterionitrobenzene and deuterioanisole, respectively (Table 1, Experiments Nos. 6-9). It is probable that in both cases the $AlCl_3$ attacks the unshared pair of electrons of the oxygen, with which $AlCl_3$ forms a stable complex. This assumption is, to some extent, confirmed by the fact that exchange was not detected between deuteriobenzene and diphenyl ether and between deuteriotoluene and dibenzyl ether (Table 1, Experiments Nos. 16-18). Such results are in complete agreement with the previously established stability of radicals attached to an oxygen atom [11].

The experiments were chiefly carried out in sealed tubes at room temperature and at 100°. The exchanging components were mixed on a mole-to-mole basis, and the amount of $AlCl_3$ used was 0.01 mole. Upon completion of the reaction, the material was washed free of $AlCl_3$ with dilute hydrochloric acid and then with water; it was then dried and separated into its components. The material was separated by ordinary distillation in Experiments Nos. 1-9 and 16, and by vacuum distillation in Experiments Nos. 17 and 18. After the distillation, traces of deuterated component II were washed out of the isolated component I. For this purpose, 15 ml of undeuterated component II was added to the component I. A second distillation was then carried out. After removal of the $AlCl_3$, the cyclohexene from Experiments Nos. 12-15 was oxidized to adipic acid by treatment with alkaline $KMnO_4$ in the cold, and in certain experiments it was brominated to dibromocyclohexane in CCl_4 at 0°. The toluene from Experiments Nos. 10 and 11 (Table 1) and 1-3 (Table 2) was isolated as benzoic acid. The purity of these products was confirmed by boiling and melting points and by mixed melting point.

The products thus identified and the original deuterium-containing material (component I) were burned in a stream of dry air over calcined cupric oxide. The water obtained from the combustion was analyzed for

deuterium content by the flotation method. The error in the measurements was 15 γ. Radiometric analysis of the material from Experiments Nos. 1-3, Table 2, was carried out on carbon dioxide with an internal gas-flow counter.

The analytical results are presented in Tables 1 and 2.

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CATALYTIC CRACKING OF SOME UNSYMMETRICAL DIARYLETHANES

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Vinylaromatic compounds of various structures may be obtained in high yields by catalytic cracking of unsymmetrical diarylethanes. This method of obtaining vinylaromatic compounds has an advantage over other methods; it consists of two stages – synthesis of the diarylethanes and cracking over silica-alumina catalyst – and, apart from an aromatic compound and acetylene, it requires no other reactants. As new processes are developed for the production of acetylene from natural gas and cracking gases, the value of diarylethanes, the synthesis of which is based on acetylene, will increase. In previous work [1, 2], we investigated the catalytic cracking of 1,1-(4,4'-dimethyl)diphenylethane and 1,1-(4,4'-diisopropyl)diphenylethane. The present paper reports the results of catalytic cracking of other unsymmetrical diarylethanes.

Catalytic cracking of 1,1-(4,4'-diethyl)diphenylethane. The 1,1-(4,4'-diethyl)diphenylethane, prepared by alkylation of ethylbenzene with acetylene and distilled twice under vacuum, had the following constants: b. p. 164-167°/10 mm, n_D^{20} 1.5562, d_4^{20} 0.9646.

25 ml of silica-alumina catalyst was placed in the catalyst tube, and 80 ml (2.6 hours^{-1} space rate) of 1,1,-(4,4'-diethyl)diphenylethane and 400 ml of distilled water was passed over the catalyst at a temperature of 550° + 5°. The catalyzate (76.12 g) was distilled in the presence of hydroquinone under vacuum in a column equivalent to 8 theoretical plates. The following fractions were obtained from the distillation: a fraction boiling at 46-49°/38 mm, 19.4 g (n_D^{20} = 1.497; 7.2% unsaturates by the Rosenmund method); a fraction boiling at 93-95°/38 mm, 31.68 g (n_D^{20} 1.5348; 87.4% unsaturates), and the residue, 31.68 g (mainly unconverted 1,1-(4,4'-diethyl)diphenylethane). The fraction boiling at 46-49°/38 mm was treated in the cold with concentrated sulfuric acid, washed, dried, and distilled at atmospheric pressure. This yielded a fraction boiling at 133-134°/748 mm, 16.2 g (n_D^{20} 1.4954; d_4^{20} 0.8679); this compound was ethylbenzene (literature data [3] for ethylbenzene n_D^{20} 1.4958, d_4^{20} 0.8670).

Mol. wt. found 105.9; calculated for C_8H_{10}, 106. MR found, 35.7; calculated, 35.54.

The fraction boiling at 93-95°/38 mm was 4-ethylstyrene containing 12.6% diethylbenzene. The 4-ethylstyrene was isolated from this fraction by means of mercuric acetate, and had the following constants: b. p. 60-61°/5 mm, n_D^{24} 1.5371, n_D^{20} 1.5379, d_4^{20} 0.8935; literature data [3]: n_D^{20} 1.5376, d_4^{20} 0.8924.

Mol. wt. found 131.3; calculated for $C_{10}H_{12}$, 132; MR found 46.2; calculated 43.61.

For complete identification of the 4-ethylstyrene, its dibromide was obtained in the form of white, acicular crystals: m. p. 65.5° (literature value [4]: m. p. 66°).

Catalytic cracking of 1,1-(3,3',4,4'-tetramethyl)diphenylethane. The 1,1-(3,3',4,4'-tetramethyl)diphenylethane (ethylidene-di-o-xylene) was prepared by alkylation of o-xylene with acetylene: b. p. 173-174°/5 mm, n_D^{20} 1.5655, d_4^{20} 0.9824. The cracking was carried out at 550°. 100 ml of 1,1-(3,3',4,4'-tetramethyl)-diphenylethane was passed over the silica-alumina catalyst (25 ml) at a space rate of 2.6 hours^{-1}. 400 ml of water was included in the feed.

The catalyzate (98 g) was distilled under vacuum in a column equivalent to 25 theoretical plates.

Three main fractions were obtained: a fraction boiling at 55-55.5°/36 mm, 22.6 g; a fraction boiling

at 94-104°/36 mm, 2.7 g; a fraction boiling at 105-106°/36 mm, 27.2 g. The fraction boiling at 55-55.5°/36 mm was o-xylene; n_D^{20} 1.5064, d_4^{20} 0.8813 (literature values [3]: n_D^{20} 1.5052, d_4^{20} 0.8802).

Mol. wt. found 107.8; calculated for C_8H_{10}, 106. MR found 35.80; calculated 35.54.

The fraction boiling at 94-104°/36 mm, a mixture of vinylxylene and ethylxylene (n_D^{20} 1.523; 46% unsaturates), was treated with concentrated sulfuric acid and distilled under atmospheric pressure. 0.8 g of a fraction boiling at 186-188° was obtained: n_D^{20} 1.5049 (literature value for 1,2-dimethyl-4-ethylbenzene [3] n_D^{20} 1.5031). The fraction boiling at 105-106°/36 mm was 3,4-dimethylstyrene: n_D^{20} 1.5465, d_4^{20} 0.9062 (literature data [5]: b. p. 94-96°/26 mm, n_D^{20} 1.5463, d_{25}^{25} 0.909).

Mol. wt. found 134.9; calculated 132. MR found 46.1; calculated 43.61.

Catalytic cracking of 1,1-di-(2-naphthyl)ethane. The 1,1-di-(2-naphthyl)ethane (dinaphthylethylene) was prepared by alkylation of naphthalene with acetylene in solution in carbon tetrachloride. It was a very viscous, transparent material with a green fluorescence. B. p. 236-238° at 3 mm; n_D^{50} 1.6760. A solution of 87 g of 1,1-di-(2-naphthyl)ethane in 60 ml of benzene was passed at a rate of 1 ml/minute through the catalyst tube, which contained 25 ml of silica-alumina catalyst. Water was fed at a rate of 4 ml/minute. The cracking temperature was 550°.

After distillation of the benzene, the catalyzate was distilled under vacuum from a Claisen flask in order to separate the cracking products from the unconverted 1,1-di-(2-naphthyl)ethane. 46.57 g of a fraction boiling at 110-150°/8 mm and 25.75 g of residue were obtained. The fraction boiling at 110-150°/8 mm consisted of crystalline and liquid fractions, and was filtered in a vacuum filter. The crystals (21.12 g) were twice recrystallized from alcohol, and, after sublimation, melted at 81-82°. They gave a picrate which melted at 148-148.5°.

Handbook data: m. p. of naphthalene 80°, m. p. of picrate 149°. The filtrate was a transparent, yellow liquid: n_D^{20} 1.636; 74.5% unsaturates.

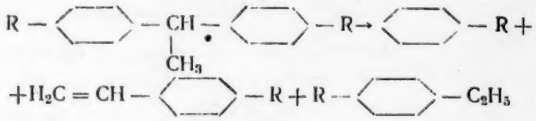
Part of the filtrate crystallized on standing. The crystals were separated, and, after several recrystallizations from alcohol, they melted at 65-65.5° (literature value for β-vinylnaphthalene [6], m. p. 66°.

Mol. wt. found 154.5; calculated for $C_{12}H_{10}$, 154.

For identification of the β-vinylnaphthalene, the filtrate was brominated at −20°. The resulting white, acicular crystals melted at 86.86.5° (literature value [7], m. p. 86°).

Mol. wt. found 315.5; calculated for $C_{12}H_{10}Br_2$, 314.

Thus the chemistry of the cracking of these diarylethanes is analogous to that of the cracking of diarylethanes in our previous work [1, 2], namely:



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DIPOLE MOMENTS OF ESTERS OF ISOMERIC 1,2-CYCLOHEXANEDICARBOXYLIC ACIDS

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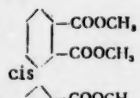
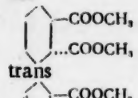
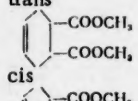
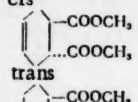
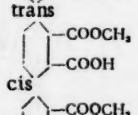
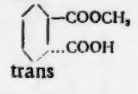
Generally, the chair-form with a maximum number of equatorial substituents is the most stable conformation. This generalization has been confirmed chiefly by a study of various cyclic compounds having methyl and hydroxyl groups as substituents.

In this connection, it seemed of interest to study compounds with more polar substituents, for example, the methyl esters of dicarboxylic acids, which have been synthesized by I. N. Nazarov and V. F. Kucherov [1, 2].

Three isomers are possible in the series of 1,2-disubstituted cyclohexanes: the cis-isomer with equatorial-axial disposition of substituents (e–a) and the trans-isomer with diequatorial (e–e) or diaxial (a–a) disposition.

TABLE 1

Expt. No.	Compound	B. p., °C/mm Hg	P_∞	F_{el}	F_{or}	$\mu \cdot 10^{18}$, D
1	 cis	110–111/5	170.43	49.26	121.17	2.41
2	 trans	135–135.5/17	144.54	49.26	95.28	2.14
3	 cis	114/5	166.76	48.79	117.97	2.38
4	 trans	136/18	140.92	48.79	92.13	2.10
5	 cis	68–69*	105.03	44.65	60.38	1.70
6	 trans	94–95*	120.48	44.65	75.83	1.91

* Melting point.

* Deceased.

In our experiments, the dielectric constant of benzene solutions was measured by the heterodyne method at 25° and at concentrations of 0.003 to 0.007 mole fraction solute. The formula of Hedestrand was used for the dipole moment calculations.

The electron polarization was calculated from bond refractions and from the experimental data. The two methods gave values which were in good agreement.

The dipole moments of ten substances – derivatives of cyclohexane and cyclohexene – were measured.

In Tables 1 and 2 are successively presented the structural formula, the boiling or melting point, the total polarization P_∞, the electron polarization P_{el}, the orientation polarization P_{or}, and the dipole moment.

The dipole moment of dimethyl cis-1,2-cyclohexanedicarboxylate was 2.41 D, while that of the trans-form was 2.14 D. The moment of the cis-form was greater by 0.27 D. The same thing was observed for the dimethyl esters of 1,2-cyclohexenedicarboxylic acids, for which μ = 2.38 D and 2.10 D for a difference of 0.28 D.

A comparison of the dipole moments of the isomers of derivatives of cyclohexane and of cyclohexene showed that the double bond introduces only an insignificant change in the dipole moment for both the cis- and the trans-forms.

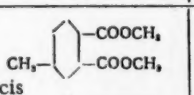
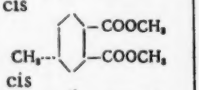
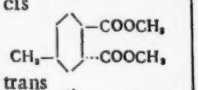
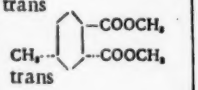
The dipole moments of the isomers of monomethyl 1,2-cyclohexanedicarboxylate were lower than those of the dimethyl esters. It is possible that this is explainable by the formation of intramolecular hydrogen bonds between the oxygen of the carbonyl group and the hydrogen of the O–H group.

It was of interest to compare the dipole moments of the isomeric methyl esters of cyclohexanedicarboxylic acid with the dipole moments of unsaturated dicarboxylic acids, for example, the diethyl esters of maleic and fumaric acids. The difference of the radicals of the ester group should not be significantly reflected in the values of the moments. Smyth and Walls [3] determined the dipole moments of the diethyl esters of maleic and fumaric acids at 25 and 50°.

	μ at 25°, D	μ at 50°, D
1. Diethyl ester of maleic acid	2.54	2.56
2. Diethyl ester of fumaric acid	2.38	2.40
3. Dimethyl ester of 1,2-cyclohexanedicarboxylic acid, cis-form	2.41	–
4. Same, trans-form	2.14	–

As may be seen from these data, the dipole moment of the ester of maleic acid is greater than the moment of the ester of fumaric acid. This is complete confirmation of the cis-configuration of compound 3.

TABLE 2

Expt. No.	Compound	B. p., °C/mm Hg	P_∞	P_{el}	P_{or}	$\mu \cdot 10^{18}$, D
1	 cis	110–110.5/4	172.83	53.88	118.95	2.39
2	 cis	105–105.5/	173.10	53.88	119.22	2.39
3	 trans	111/5	160.53	53.88	106.65	2.26
4	 trans	110–110.5/4	157.32	53.88	103.44	2.23

In Table 2 are presented the dipole moments of compounds which, in contrast to the previously considered compounds, have an additional methyl group at the number 4 ring carbon.

Identical moments were obtained for isomers 1 and 2. This would be expected, since the moment of the CH_3 group is equal to that of a C–H bond. Isomers 3 and 4 have somewhat lower moments. We note that isomer 4 is the most stable; the remaining forms convert to it. Tulinsky, Di Giacomo and Smyth [4], Kozima and co-authors [5], and Bender, Dervin, Flowers and Goering [6] all calculated the content of diequatorial and diaxial isomers of dihalocyclohexanes in solutions of the trans-compounds using a formula for mixtures which assumes that the moment of the diaxial isomer is zero. For substituents of the type present in the esters of 1,2-cyclohexanedicarboxylic acids, which contain skewed groups, the moment of the diaxial isomer (a–a) cannot be taken as zero.

In order to determine the configuration of the isomers of the dimethyl 1,2-cyclohexanedicarboxylates, calculations of the dipole moments were carried out assuming free rotation of the $COOCH_3$ groups and taking into account their direction as skewed groups with respect to the cyclohexane ring. The data of Smyth [7] were used for the bond moments, the angle of rotation, and the vector angle of the moment of the skewed $COOCH_3$ group. The calculations were carried out by means of the formula:

$$\mu^2 = (\underset{\rightarrow}{\Sigma}\mu_i')^2 + \Sigma(\mu_i'')^2,$$

where i is the index of the group with a moment μ_i. The moments μ_i were resolved into the components μ_i' – parallel to the axis of rotation – and μ_i'' – perpendicular to this axis. The arrow under the first summation denotes that the moments μ_i' were summed vectorially

$$\underset{\text{and } e-e}{\mu_{e-a}} = \sqrt{(2\cdot 1.74\cos 70^\circ\cdot\cos 35^\circ)^2 + 2\cdot 1.74^2\cdot\sin^2 70^\circ} = 2.51 \text{ D.}$$

The moment of the a–a isomer was calculated by the equation

$$\mu_{a-a} = \sqrt{2(1.74\cdot\sin 70^\circ)^2} = 2.30 \text{ D.}$$

The value 1.74 is the moment of the $COOCH_3$ group [7]. The experimental value of the cis-isomer lies between the calculated values 2.51 and 2.30 D.

The experimental moment of the trans-isomer, 2.14 D, does not correspond to the moment calculated for the e–e isomer assuming free rotation.

We note that the moment of the dimethyl ester of terephthalic acid, 2.2 D [9], indicates a slight restriction of rotation.

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SYNTHESIS OF ALKYLATED HYDROPEROXIDES OF THE 1,1-DIPHENYLETHANE SERIES AND THE USE OF CHROMATOGRAPHY FOR THEIR RECOVERY

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(Presented by Academician B. A. Arbuzov, October 5, 1957)

The chemistry of organic peroxide compounds has recently been enriched by the addition of many new hydroperoxides obtained by autooxidation of hydrocarbons of almost all of the various series. Previous work [1-3] has established certain rules of the autuooxidation process, namely, that peroxidation proceeds predominantly at a C—H bond, and the reactivity of this bond increases both as the C atom changes from primary to secondary to tertiary and under the influence (through the α-carbon atom) of other structural factors such as ester oxygen, a benzene ring, a double bond, a system of double bonds, etc. Our previous work [4, 5] has shown that, in the series purely alkyl, $(CH_3)_3COOH$, alkyl-aryl, $C_6H_5(CH_3)_2COOH$ and $(C_6H_5)_2CH_3COOH$, and purely aryl, $(C_6H_5)_3COOH$, the rate of thermal decomposition and the correspondingly varying initiating activity are increased by the influence of phenyl radicals, and they are optimized in 1,1-diphenylethane hydroperoxides.

In this connection, it was of interest to clarify the effect on the autooxidation process and on the properties of the hydroperoxides of various alkyl radicals acting through a benzene ring on the C—H bond and on the —OOH hydroperoxide group. Therefore, the problem arose of synthesizing several hydroperoxides of the 1,1-diphenylethane series containing the following alkyl radicals in a para position in one of the benzene rings CH_3 (I), C_2H_5 (II), $CH(CH_3)_2$ (III), and $C(CH_3)_3$ (IV), and also a hydroperoxide in which the n-C_3H_7 (V) group was joined to the bridging carbon atom. The formulas are presented below):

The enumerated hydroperoxides were prepared by autooxidation of the corresponding hydrocarbons, and were separated from the unreacted hydrocarbon and purified by chromatography, since distillation and crystallization could not be used.

The hydrocarbons p-$CH_3C_6H_4CH(CH_3)C_6H_5$ (1), p-$C_2H_5C_6H_4CH(CH_3)C_6H_5$ (2), p-$(CH_3)_2CHC_6H_4CH(CH_3)C_6H_5$ (3) and p-$(CH_3)_3CC_6H_4CH(CH_3)C_6H_5$ (4) were synthesized by the method of Kraemer and co-workers [6] by condensation of styrene with the appropriate alkylbenzenes, toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene, in the presence of sulfuric acid. The hydrocarbons were washed with concentrated sulfuric acid, 30% alkali, and water, and were distilled under vacuum. Of the previously undescribed hydrocarbons (2), (3), and (4), in the interests of accuracy the latter two were also prepared by organomagnesium synthesis; (3) was prepared from p-bromocumene and acetophenone through phenyl-p-cumylmethylcarbinol with subsequent reduction of the latter to the hydrocarbon; the synthesis of (4) has been described in reference [7]. The hydrocarbon, 1,1-diphenyl-n-butane, used in the preparation of hydroperoxide V, was obtained by the method of Klages and Heilman [8] from propyl bromide and benzophenone through diphenylpropylcarbinol with subsequent reduction to the hydrocarbon. Data characterizing these hydrocarbons are presented in Table 1.

TABLE 1

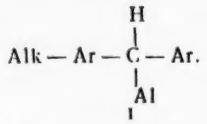
Hydrocarbon	B. p., °C (2-3 mm Hg)	d_4^{20}	n_D^{20}	MR		C, %		H, %	
				found	calc.	found	calc.	found	calc.
1	115–116	0.9850	1.5660	64.77	64.27	—	—	—	—
2	118–119	0.9743	1.5610	68.89	69.89	91.06	91.38	8.78	8.63
3	137–139	0.964	1 5530	75.24	73.50	90.76	91.01	9.16	8.99
4	148–150	0.960	1.5508	78.88	78.12	84.82	84.99	8.70	8.72
5	86 m.p. 27	—	—	—	—	—	—	—	—

The autooxidation of the hydrocarbons was carried out in a glass flask at a temperature of 80-82° and in the presence of an 0.1 N solution of sodium hydroxide which was present in a ratio of hydrocarbon to aqueous phase of 1:1; pure oxygen was bubbled through the mixture at a rate of 6-8 ml/minute. The rate and degree of accumulation of hydroperoxide (hp) are shown in Table 2.

TABLE 2

Hydrocarbon	Run 1			Run 2			Run 3			Run 4		
	time, hours	HP, %	rate of accumulation, % hour	time, hours	HP, %	rate of accumulation, % hour	time, hours	HP, %	rate of accumulation, % hour	time, hours	HP, %	rate of accumulation, % hour
1	24	3.56	0.15	48	11.84	0.36	67	16.17	0.23	96	25.0	0.30
2	24	4.6	0.19	48	13.0	0.36	72	20.5	0.31	—	—	—
3	46	3.6	0.08	88	15.5	0.30	158	44.4	0.41	222	53.4	0.14
4	48	5.2	0.11	96	23.0	0.16	165	42.2	0.28	214	53.3	0.23
5	48	7.0	0.15	72	12.7	0.24	120	15.0	0.05	—	—	—

It is seen from these results that under the conditions used, all of the hydrocarbons substituted in the para position in one of the benzene rings underwent autooxidation at roughly the same rate, namely, at a maximum rate of formation of hydroperoxide of 0.25-0.35% per hour. This observation is in agreement with the fact that all of the structures (I) are the same.



It follows from these results that the specific alkyl radical introduced into the para position of one of the benzene rings has essentially no effect on a peroxidation process occurring at the site of a tertiary C–H bond. A peculiarity is that during the autooxidation of hydrocarbons 3 and 4 there was a more prolonged induction period; this is apparently connected with the purification, and not with the structure, of these hydrocarbons. Hydrocarbon 5 behaved differently in that during its oxidation the accumulation of hydroperoxide did not proceed to an extent greater than 14-15%, since further oxidation resulted in almost complete decomposition of the hydroperoxide. Apparently, the decrease in thermal stability of the hydroperoxide is connected with the increase in the length of the aliphatic chain at the tertiary carbon atom.

The hydroperoxides were separated and purified from the oxidized hydrocarbons by a chromatographic method [7] in which aluminum oxide of decreased activity (between II and III on the Brockmann scale) was

used as the adsorbent, petroleum ether (35-70°) was used as the solvent, and diethyl ether was used as the desorbent. The oxidized hydrocarbons were first washed with a 5% solution of sodium hydroxide and then with water, and were dried under vacuum until clear. The oxidized and washed hydrocarbons were then diluted with petroleum ether to a hydroperoxide content of 5-6%, and were passed through a chromatographic column at a rate of 0.30-0.35 ml/minute to saturation (control was by the iodometric method). After the adsorbent had been washed with pure solvent, the hydroperoxides were desorbed with diethyl ether, and, after distillation of the ether, 97-98% hydroperoxide was obtained which, after a second passage through the column, was pure. In Table 3 are presented data characterizing the freshly prepared hydroperoxides.

TABLE 3

Hydroperoxide	M. p., °C	d_4^{20}	n_D^{20}	MR		C, %		H, %		O_2, %	
				found	calc.	found	calc.	found	calc.	found	calc.
I	Liq.	1.123	1.5820	67.80	67.98*	78.82	78.91	7.38	7.09	7.01	7.01
II	Liq.	1.101	1.5755	72.82	72.60	79.10	79.31	7.68	7.46	6.63	6.61
III	Liq.	1.079	1.5670	77.41	77.22	79.63	79.15	7.92	7.86	6.24	6.24
IV	47	—	—	—	—	80.38	79.96	8.15	8.20	5.91	5.92
V	39	—	—	—	—	79.25	79.33	7.50	7.43	6.60	6.61

* The contribution of the peroxide group, —OO—, was taken as 3.715 [1, 9].

These hydroperoxides were also characterized chemically by their decomposition products. Decomposition of (I) over highly active aluminum oxide gave acetophenone (semicarbazone m. p. 195.5°) and p-cresol (bromo derivative m. p. 48-49°). Decomposition of (II) by the method of Kharasch [10] in glacial acetic acid and in the presence of perchloric acid gave acetophenone and p-ethylphenol (m. p. 44-47°). Decomposition of (III) over active aluminum oxide gave acetophenone and p-isopropylphenol. Reduction of (IV) with potassium iodide in glacial acetic acid gave the corresponding carbinol (m. p. 86°), from which the original hydrocarbon was obtained by organomagnesium synthesis. Decomposition of (IV) over aluminum oxide gave acetophenone and p-tert-butylphenol (bromo derivative m. p. 49-50°). Reduction of (V) under the same conditions gave the carbinol (m. p. 65°, the same as that of the carbinol from which the hydrocarbon was orginally prepared). It is interesting that no phenol was formed during decomposition of (A) over active aluminum oxide, and the hydroperoxide decomposed to benzophenone only.

These data lead to the conclusion that the peroxide compounds synthesized by us were tertiary hydroperoxides, the structures of which are expressed by the formulas given above, and they can accordingly be assigned the following names. I: 1-phenyl-1-p-tolylethane-1-hydroperoxide; II: 1-phenyl-1-p-ethylphenylethane-1-hydroperoxide; III: 1-phenyl-1-p-cumylethane-1-hydroperoxide; IV: 1-phenyl-1-(4-tert-butylphenyl)ethane-1-hydroperoxide; V: 1,1-diphenyl-n-butane-1-hydroperoxide.

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THE PREPARATION OF HALOMETHYL DERIVATIVES OF ALUMINUM BY THE DIAZOALKANE METHOD

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(Presented by Academician A. N. Nesmeianov, November 22, 1957)

It is well known from the literature [1-8] that aliphatic diazo compounds can be successfully used for the synthesis of heteroorganic compounds. Systematic investigations along this line are exemplified by the work of A. Ia. Iakubovich and co-workers [2-6], who, using this method, developed means for the preparation of organic compounds of the elements of Groups IV and V of the periodic system.

Thallium [9] and boron [10] are the only elements of Group III of the periodic system for which organic compounds have been prepared by the diazoalkane method.

It seemed of interest to extend this method to the preparation of halomethyl derivatives of aluminum – compounds which have not been described in the literature.

The action of diazomethane on aluminum fluoride, chloride, and bromide was studied in the present work.

Considering that the action of diazomethane on boron and thallium halides yields fluoromethylboron difluoride and di(chloromethyl)thallium chloride, it would be expected that the mono or dihalomethyl derivative would be formed in the case of aluminum. However, these derivatives were not detected even in the case when the diazomethane and aluminum halide were used in a ratio of 1:3.

In all cases, we obtained only the tri(halomethyl)aluminum. The reaction apparently proceeds according to:

$$AlX_3 + 3CH_2N_2 \rightarrow Al(CH_2X)_3 + 3N_2,$$

where X = Cl or Br.

In such reactions, alkenylation of all of the halogen atoms in the halide of an element is known both for arsenic and antimony (in which case the trihalodialkyl derivatives are obtained) and for tin (in which case the tetrahalodialkyl derivatives are obtained). But in all of these cases there was a mixture of all possible derivatives, i.e., the mono- di-, tri-, and tetrahaloalkyl derivatives, the formation of which was dependent on the ratio of the amounts of aliphatic diazo compound and halide of the respective element. In the case of aluminum, we obtained only the trihalomethyl derivative regardless of the amounts of initial reagents used in the reaction.

Aluminum chloride and bromide reacted vigorously with diazomethane even at a temperature of –50°; this may be contrasted to the behavior of aluminum fluoride, which did not enter into the reaction even at room temperature. The addition of "copper bronze" into the reaction mixture as a catalyst caused decomposition of the diazomethane. The sole product was "polymethylene," since the aluminum fluoride was recovered unchanged from the reaction mixture.

Since the action of diazomethane on the halides of elements consists of the introduction of an "alkylene" biradical between the halogen and the element, the rate of this reaction depends on the energy of the E–X bond, other conditions being the same. Thus, the reaction proceeds more easily when X is chlorine or bromine and more difficultly when X is fluorine.

Tri(chloromethyl)aluminum and tri(bromomethyl)aluminum are crystalline substances which fume strongly in air and which are very hygroscopic. They are readily oxidized, and, therefore, all operations during their preparation were carried out in a stream of dry and oxygen-free nitrogen. These substances are unstable, especially the bromo derivative (even when sealed up under a stream of nitrogen, it darkens and decomposes after several days), and are soluble in cold ether and less soluble in benzene. They react vigorously with cold water, decomposing and forming hydrogen chloride or, correspondingly, hydrogen bromide, aluminum hydroxide, and methyl alcohol. All of these substances were identified by means of well-known qualitiative analytical reactions characteristic of them.

TABLE 1

Experiment No.	Amount of starting material, g			Yield (in g above line and in % below line)	
	CH_2N_2	$AlCl_3$	$AlBr_3$	$Al(CH_2Cl)_3$	$Al(CH_2Br)_3$
1	3	9.4	19.0		
2	3	3.1	6.3	3.0 72.0	2.7 36.9

The ethereal solution used in the syntheses was dried by chilling to –70° over KOH and then by allowing it to stand over sodium wire. The amount of diazomethane was determined by titration. The aluminum chloride and bromide used in the reaction were also anhydrous. The reaction was carried out by two methods. The aluminum chloride or bromide was added in three portions to the ethereal solution of diazomethane, which was cooled to –50°. A vigorous reaction occurred, the temperature of the solution rose to +10°, and the solution became colorless. The second method differed from the first in that the cooled ethereal solution of diazomethane was added dropwise, with stirring, and over a period of an hour to a solution of the aluminum halide in ether at –50°. The same product – tri(chloromethyl)aluminum or tri-(bromomethyl)aluminum – was obtained in approximately the same yield in both cases.

After filtration of the excess aluminum halide from the solution* and removal of the solvent under vacuum and in a stream of nitrogen, the residue was vacuum distilled using traps cooled to –70° to collect possible lower fractions. The distillation yielded a pale yellow liquid material, which rapidly crystallized in the receiver and which was the pure product.

TABLE 2

Substance	B. p., °C/mm Hg	M. p., °C	C, %		H, %		Al, %		Halogen, %	
			found	calc.	found	calc.	found	calc.	found	calc.
$Al(CH_2Cl)_3$	108–109/1.5	32–33	20.54	20.84	3.45	3.64	15.37	15.15	60.64	60.26
	128–129/4.5			20.91		3.83		14.84		59.75
$Al(CH_2Br)_3$	119–120/0.7	47–48	11.67	11.52	1.96	1.64	8.73	8.43	77.64	77.44
	132–133/2			12.00		1.86		8.06		76.76

In Table 1 are presented the data on the amounts of starting materials used in the reactions and on the yields of pure compounds. The yields were calculated on the basis of the diazomethane. In Table 2 are presented the physical constants of the pure materials and the results of their analyses.

* Only when using the first method was it necessary to filter the ethereal solution, since under the conditions of this method, a part of the aluminum chloride (and especially of the aluminum bromide) became insoluble; the solution was filtered at 0-5°.

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THE SYNTHESIS OF INFUSIBLE BUT SOLUBLE POLYMERS

Corresponding Member AN SSSR K. A. Andrianov, A. A. Zhdanov and E. Z. Asnovich

Such very important properties of polymers as their ability to melt* and to dissolve in organic solvents must be considered to be connected and to be dependent on the structure of the molecular chain of the polymer. It is well known that polymers with a linear molecular structure are soluble in organic solvents and melt on heating regardless of molecular weight. Branching of the polymer chain, i.e., branching with cross-linking and the development of a three-dimensional structure, leads to the loss of polymer solubility and the ability to melt.

Such a connection between the structure of the molecular chain and solubility and melting is observed in all known polymers. A considerable effect on the indicated properties of linear polymers is exerted by hydrogen bonds (as, for example, the limited solubility of certain representatives of polyamides with a linear structure) or stiffness and packing density of the chains (as in polytetrafluoroethylene). Nevertheless, the connection among melting, solubility, and structure of the molecular chain is retained in these cases.

There is no description in the literature of polymers which are soluble in nonpolar or weakly polar solvents but which would not melt on heating. We undertook attempts to synthesize such polymers. During the course of the investigation, it became more and more apparent that it is possible to synthesize polymers having no such connection between solubility and melting as have presently known polymers. After thorough investigations among certain classes of polymers, it was found that polymers with the indicated properties could not be obtained from the cyclic polyorganosiloxanes. Hydrolysis of phenyltrichlorosilane in aqueous acid media established that the polymers had the overall composition $(C_6H_5SiO_{1.5})_x$.

This composition corresponds to a molecule with a cyclic structure. However, such polymers dissolve in aromatic solvents and melt on heating. Hydrolysis of completely chlorinated phenyltrichlorosilane led to a product having the composition $(C_6Cl_5SiO_{1.5})_6$ and a more complex cycle structure; it was readily soluble and melted at 210-215°. Hexaethylcyclosiloxane, $(C_2H_5SiO_{1.5})_6$, and octaethylcyclosiloxane, $(C_2H_5SiO_{1.5})_8$, [1] have been prepared, but they, too, melted and were soluble.

Lengthy heating of cyclic polyphenylsiloxanes at temperatures of 250° and higher leads to an increase in the melting point, but the polymer simultaneously loses its solubility. It is probable that growth of the polymer molecule proceeds chiefly by opening of the rings and their polymerization with the formation of a cross-linked structure.

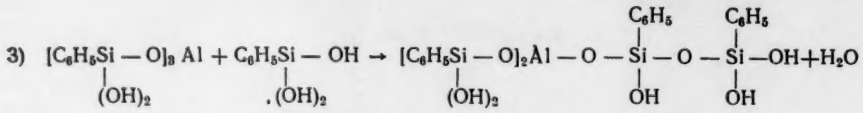
In order to increase the melting point of cyclic polyphenylsiloxanes, aluminum was introduced into the polymer molecule. It was believed that this would sharply decrease the stiffness of the polymer chain and thereby increase the melting point. The synthesis of this polymer – polyaluminophenylsiloxane – was carried out according to the following reaction scheme:

$$1)\quad 3C_6H_5Si(OH)_2ONa + 0.5Al_2(SO_4)_3 \rightarrow [C_6H_5Si(OH)_2O]_3Al + 1.5Na_2SO_4$$

$$2)\quad C_6H_5Si(OH)_2ONa \xrightleftharpoons{H_2O} C_6H_5Si(OH)_3 + NaOH.$$

* Polymers melt over a certain temperature range rather than at a specifically determined temperature.

The aluminosiloxane reacted with phenyltrihydroxysilane with the elimination of water:



Further condensation then proceeded at the expense of the hydroxyl groups to form a polymer with an average molecular weight of 5990, a hydroxyl group content of 5.5%, and a ratio of silicon to aluminum of 4.1.

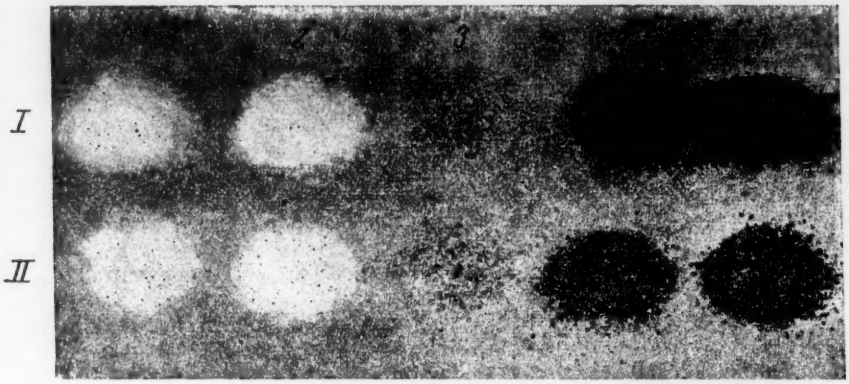


Fig. 1. The change in polyaluminophenylsiloxane (I) and in polyaluminoethylsiloxane (II) on heating: 1) original resin, 2-5) test samples; 2) 200°, 10 hours; 3) 300°, 15 minutes; 4) 400°, 15 minutes; 5) 500°, 15 minutes.

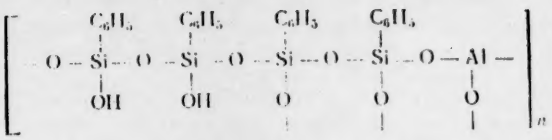
The polyaluminophenylsiloxane prepared in this manner was a colorless, brittle, glassy product which did not melt on heating.

It is seen from Fig. 1 that the powdered polyaluminophenylsiloxane neither melted nor sintered at temperatures up to 500°. It was readily soluble in benzene, toluene, acetone, ethyl alcohol, chlorobenzene, and carbon tetrachloride, but it did not dissolve in petroleum ether or white spirit. On evaporation of the solvent the polymer formed films which were soluble in the same solvents if they were not heated at a high temperature.

A study of the solubility of the polymer showed that it did not lose its solubility on heating at 150° for 10 hours (Table 1), although the hydroxyl group content decreased during the heating from 5.53 to 2.7%.

The polyaluminophenylsiloxane retained its solubility in acetone after being heated at 200° for 4 hours, and it was soluble to the extent of 85% after heating at 300° for 15 minutes. The polymer completely lost its solubility when heated for a longer time at 200° or when heated for 15 minutes at 400 or 500°. Chemical analysis of the polyaluminophenylsiloxane and determination of the molecular weight [2] showed that the elemental composition, in weight %, was: C, 49.18 and 49.35; H, 4.28 and 4.18; Si, 18.88 and 18.15; Al, 4.14 and 4.39; hydroxyl groups, 5.53. This corresponds to Si/Al = 4.1, C/Si = 6.19, and H/C = 1.0. The molecular weight of the infusible polyaluminophenylsiloxane was 5990. Fractional precipitation of the polymer from carbon tetrachloride with petroleum ether gave fractions for which the minimum molecular weight was 2770 and the maximum was 11,800.* The reactions involved in the formation of the polymer and the chemical composition of the polymer correlate with a chain having the empirical formula:

* The molecular weight determinations were carried out by S. R. Rafikov and I. I. Tverdokhlebova.



It is easy to see that such a molecular chain unit is a component part of a complex cyclic or three-dimensional polymer molecule. The solubility and low molecular weight of the polymer excludes a proposal of a three-dimensional structure for the molecule. A cyclic structure of the polymer molecule readily explains the high solubility of the polymer in ordinary organic solvents. Polyaluminoethylsiloxane was prepared from the monosodium derivative of ethyltrihydroxysilane and potassium alum by the same reaction scheme: like the polyaluminophenylsiloxane, the polymer was colorless, brittle, and glassy. The polyaluminoethylsiloxane had the same properties as the polyaluminophenylsiloxane; it did not melt on heating (Fig. 1), but did dissolve in carbon tetrachloride, chlorobenzene, acetone, ethyl alcohol, and toluene.

TABLE 1

Solubilities of Polyaluminophenylsiloxane and of Polyaluminoethylsiloxane (in per cent)

Solvent	100°	150°	200°			300°	400°	500°
	10 hours		2 hours	4 hours	10 hours	0,25 hours		
Polyaluminophenylsiloxane								
Toluene	100	100	11	4	Insoluble	2	Insoluble	Insoluble
Ethanol	100	100	100	91	" "	31	2	" "
Acetone	100	100	100	100	2	85	3	" "
Chlorobenzene	100	100	47	7	Insoluble	5	Insoluble	" "
Polyaluminoethylsiloxane								
Ethanol	100	90	3	Insoluble		7	Insoluble	Insoluble
Acetone	100	100	4	" "		10	" "	" "

In Table 1 is presented the solubility of polyaluminoethylsiloxane in ethyl alcohol and in acetone after it has been heated at different temperatures.

The polyaluminoethylsiloxane loses its solubility more rapidly than does the polyaluminophenylsiloxane. This is probably explained by a more rapid conversion of the polyaluminoethylsiloxane to an insoluble product by cleavage of the ethyl radical at the silicon atom and the formation of a siloxane bond.

Thus, polyaluminophenylsiloxane and polyaluminoethylsiloxane were synthesized by a double decomposition reaction; these polymers were readily soluble in nonpolar or weakly polar organic solvents and did not melt at temperatures up to 500°.

Polyaluminoethylsiloxane and polyaluminophenylsiloxane have molecules with a complex cyclic structure. In contrast to known polymers having a linear or cross-linked and three-dimensional structure, there is no connection between the solubility and fusibility of these polymers. These polymers are readily soluble in organic solvents, but their melting point is higher than the decomposition temperature, as is the case with infusible polymers having a three-demensional molecular structure.

EXPERIMENTAL

The following were used in the work: phenyltrichlorosilane with a chlorine content of 50.0% (50.31%), ethyltrichlorosilane with a chlorine content of 65.1% (65.08%), GOST 4328-48 analytical grade sodium hydroxide, GOST 3758-47 analytical grade aluminum sulfate, and GOST 4329-48 analytical grade potassium alum.

Hydrolysis of phenyltrichlorosilane. With vigorous stirring, phenyltrichlorosilane was introduced into water contained in a glass hydrolyzer having a double wall for the circulation water and fitted with a mechanical stirrer, a dropping funnel, and a thermometer. The temperature in the hydrolyzer was 20-25°. After the introduction of all of the phenyltrichlorosilane, stirring was continued for another 30 minutes to the completion of the reaction. The resulting polyphenylsiloxane was washed to a neutral reaction toward Congo red.

Polyaluminophenylsiloxane. The reaction was carried out in a glass, three-necked, round-bottomed flask fitted with a dropping funnel, a mechanical stirrer with an oil seal, a reflux condenser and a thermometer. 25.8 g of polyphenylsiloxane and 8 g (0.2 mole) of a 20% aqueous solution of sodium hydroxide were placed in the flask; the temperature was 20°. On mixing of the reagents, the temperature in the reaction medium rose to 28°. The reaction mixture was then heated to 70-75°, and 16.63 g (0.025 mole) of a 20% aqueous solution of aluminum sulfate was added in a fine stream to the reaction mixture. After the introduction of the aluminum sulfate, the contents of the flask were heated at 70-75° for 2 hours. The reaction was carried out in an aromatic hydrocarbon-water medium. At the completion of the reaction, the organic layer was separated from the aqueous layer and was washed with water until free of SO''_4; the washings were tested for sulfate with barium chloride. The excess solvent was distilled at a temperature of 35-40° and a residual pressure of 20-25 mm Hg. The polymer was finally dried of solvent at 15 mm Hg and 110° over a period of 1.5 hours. The yield of polyaluminophenylsiloxane was 80% of theoretical.

Found %: C 49.18, 49.35; H 4.28, 4.18; Si 18.88, 18.15; Al 4.39, 4.14; OH 5.53. $[C_{24}H_{22}Si_4AlO_{8.5}]_n$.
Calculated %: C 49.25; H 3.76; Si 19.15; Al 4.6; OH 5.81.

The molecular weight (ebullioscopic, in benzene) was 5990. The molecular weight calculated for $C_{24}H_{22}Si_4AlO_{8.5}$ is 585, and, therefore, the value of n is 10.

Polyaluminoethylsiloxane. This polymer was synthesized similarly from 25 g of polyethylsiloxane, 12.3 g (0.31 mole) of sodium hydroxide, and 29.2 g (0.062 mole) of potassium alum. The yield of polyaluminoethylsiloxane was 76% of theoretical.

Found %: Si 28.15, 27.61; Al 5.6, 5.92. $[C_{10}H_{27}Si_5AlO_{10}]_n$. Calculated %: Si 29.5; Al 5.7.

The molecular weight (ebullioscopic, in benzene) was 1020. The molecular weight calculated for $C_{10}H_{27}Si_5AlO_{10}$ is 474, and, therefore, n is 2.

Solution of the polymers. Solution of the original polymers and of those subjected to heating at various temperatures was carried out as follows: in all cases, 0.5 g of polymer and 9.5 g of solvent (calculated for the preparation of a 5% solution), were used. Solution was carried out in small flasks with ground glass stoppers. The polymers were in contact with the solvent for 24 hours at 20°. During this time, the flasks were shaken three times: a) at the beginning of the experiment, b) after 19 hours, and c) after 24 hours. Following this, the amount (in %) of polymer in solution was determined.

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ALKYLATION OF NAPHTHALENE, β-METHYLNAPHTHALENE AND TETRALIN WITH ACETYLENE

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(Presented by Academician A. V. Topchiev, October 8, 1957)

The alkylation of naphthalene with acetylene has been studied by Reilly and Nieuwland [1]. They showed that naphthalene and other polynuclear hydrocarbons, such as biphenyl, diphenylmethane, bibenzyl, and triphenylmethane, are not alkylated when sulfuric acid and mercuric oxide are used as the catalyst. Reilly and Nieuwland attempted to explain the fact that naphthalene is not alkylated under these conditions on the basis that the naphthalene molecule is similar to a benzene derivative with an unsaturated radical in a side chain.

Other investigators [2] also consider the naphthalene molecule as consisting of two rings, one an aromatic ring and the other an alicyclic ring.

In our opinion, naphthalene is not alkylated by acetylene under these conditions, because the naphthalene molecule, which consists of two aromatic rings, is a stable molecule. According to Fries' rule, the most stable form of polynuclear compounds is the form which has the greatest number of rings with the normal structure of the benzene ring (i.e., with three double bonds, and not two as in the case of a quinoid structure).

It is also possible to assume that the solvent has a predominant effect in alkylation reactions. On this basis, we attempted to alkylate naphthalene in alcoholic solution using $H_3PO_4 \cdot BF_3$ as the catalyst; this attempt was based on the assumption that the alkylation of naphthalene proceeds similarly to that of β-naphthol [3]. However, the attempt was unsuccessful; after the acetylene had been passed into the naphthalene solution for three hours at various temperatures and after appropriate treatment of the raw alkylate, only pure naphthalene was distilled.

Subsequently, we were led to try other solvents – chloroform and carbon tetrachloride. Naphthalene was alkylated under these conditions.

Alkylation of Naphthalene

The naphthalene solution, the catalyst, and 1-2 g of mercuric oxide, were placed in a reactor with a mechanical stirrer. The experiments were carried out at a temperature of 50-55°. The acetylene was fed from a cylinder at a rate of 3 liters/hour. The raw alkylate was dissolved in ether, and the ether extract was neutralized with soda, washed with water, and dried with calcium chloride. After distillation of the ether, the residue was distilled under vacuum. The main product was obtained at a temperature of 243-245° and a pressure of 5 mm Hg or at 236-238° and 3 mm Hg.

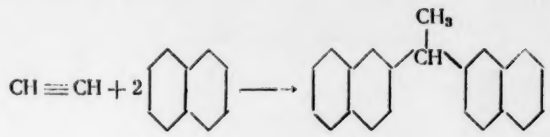
The results are presented in Table 1.

Optimum reaction conditions were a temperature of 50-55°, a catalyst concentration of 16%, and a mole ratio of naphthalene to acetylene of ~1.0.

At room temperature, the alkylate was a very light yellow, solidified, transparent mass which was soluble in benzene, chloroform, and ether.

Mol. wt., found 279, 287; calculated for ethylidene-bis-naphthalene [1,1-dinaphthylethane], $C_{22}H_{18}$, 282.

The reaction proceeded according to the equation



The molar refraction of this compound was determined in benzene solution. MR, found 91.5; calculated for $C_{22}H_{18}$, 90.3.

Attempts to carry out oxidation of the alkylate for identification purposes were unsuccessful; the oxidation products were a mixture of difficultly separable aromatic acids. The structure of the $C_{22}H_{18}$ was confirmed by cracking the product. A solution of $C_{22}H_{18}$ in benzene was passed over aluminosilicate catalyst at a temperature of 550° and in the presence of steam as a diluent. White crystals of β-vinylnaphthalene were isolated from the cracking products as thin leaves with a m. p. of 65-65.5° (literature value, 66° [4]); α-vinylnaphthalene was not detected in the cracking products.

In accordance with our investigations [5, 6] of cracking products, it was possible to identify the $C_{22}H_{18}$ as ethylidene-bis-β-naphthalene [1,1-di(β-naphthyl)ethane].

TABLE 1

Expt. No.	Napthalene, g	Solvent*, ml	Catalyst		Acetylene, g	Mole ratio naphthalene : acetylene	Alkylate	
			ml	% in reaction mixture			g	% of theoretical
1	40	25	20	33	8.7	0.9	16	36
2	40	50	20	28	10.4	0.8	17	39
3	40	40	10	16	10.4	0.8	17	39
4	40	40	5	9	10.4	0.8	15	34
5	120	120	30	16	32	0.8	53	40

* Chloroform in Experiment 1, CCl_4 in Experiments 2-5.

Alkylation of β-methylnaphthalene. β-Methylnaphthalene (m. p. 31.5°), similarly to naphthalene, was alkylated with acetylene at a temperature of 50-55°; chloroform and carbon tetrachloride were used as solvents.

The experimental results are presented in Table 2.

TABLE 2

Expt. No.	Methylnaphthalene, g	Solvent*, ml	Catalyst		Acetylene, g	Mole ratio naphthalene : acetylene	Alkylate	
			ml	% of reaction mixture			g	% of theoretical
1	30	20	20	39	10.4	0.5	7	21
2	40	40	20	28	7	1.0	9	21
3	40	40	10	16	7	1.0	14	33
4	40	40	5	9	7	1.0	7	17

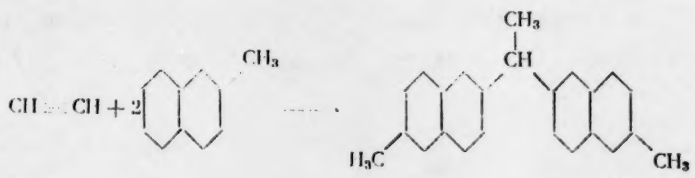
*Chloroform in Experiment 1, CCl_4 in Experiments 2-4.

The optimum reaction conditions were the same as those for the alkylation of naphthalene.

The resulting alkylate, after appropriate treatment, was distilled under vacuum. The major product distilled at a temperature of 262-265° and a pressure of 5 mm Hg.

Mol. wt., found 308, 308; calculated for $C_{24}H_{22}$, 310.

This hydrocarbon, ethylidene-bis-β-methylnaphthalene [1,1-di-(6-methylnaphthyl)ethane], was formed according to



This hydrocarbon, a thick, viscous liquid with a greenish color, was soluble in benzene, chloroform, carbon tetrachloride, and n-heptane, and insoluble in alcohol.

Alkylation of tetralin. Tetralin, b. p. 72-74°/4 mm, was also alkylated. The results of the experiments, which were carried out in carbon tetrachloride solution at 60-65°, are presented in Table 3.

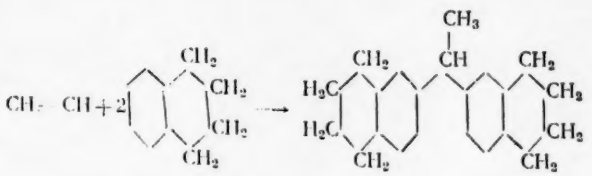
TABLE 3

Expt. No.	Tetralin, g	Solvent, ml	Catalyst		Acetylene, g	Mole ratio tetralin : acetylene	Alkylate	
			ml	% of mixture			g	% of theoretical
1	40	20	10	21	10.4	0.8	18	41
2	40	20	5	12	10.4	0.8	14	32

The optimum conditions and alkylate yield in this reaction were approximately the same as in the alkylation of naphthalene.

The resulting alkylate had a b. p. of 214-216°/5 mm.

Mol. wt., found 288, 288; calculated for ethylidene-bis-tetralin, $C_{22}H_{26}$, 290. The ethylidene-bis-tetralin was formed according to



This compound was a thick, viscous liquid with a pale yellow color; it was soluble in benzene, chloroform, and n-heptane, and insoluble in alcohol.

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X-RAY STRUCTURAL INVESTIGATION OF NAPHTHAZARINE

G. A. Gol'der and G. S. Zhdanov

(Presented by Academician N. V. Belov, November 20, 1957)

Among the hydroxyketone dyes which are derivatives of naphthoquinone, naphthazarine (5,8-dihydroxy-1,4-naphthoquinone) has found widespread acceptance. X-ray methods were first used for the study of napththazarine by Palacios and Salvia [1], who established for this compound a monoclinic cell with the dimensions: a = 3.85, b = 8.02, c = 14.5 A, the angle $\beta = 97°, 6'$; Z = 2, and the space group is $C_{2h}^5 = P2_1/n$. In order to harmonize the presence of a center of symmetry in the molecule, which followed from the x-ray data, with the structure shown as Formula I, Palacios and Salvia proposed that the hydrogen atom oscillated between the neighboring oxygen atoms of the two nuclei.

Banarjee [2], investigating the magnetic anisotropy of naphthazarine, considered that his value for the magnetic susceptibility could not be brought into conformity with the presence of two molecules in the unit cell, and he proposed that the unit cell contained four noncentrosymmetric molecules. His values of the magnetic susceptibility were $K_1 = K_2 - 60.7 \cdot 10^{-6}$ and $K_3 = -132.8 \cdot 10^{-6}$. Billy [3] investigated the structure of naphthazarine in another modification (2), the dimensions of the unit cell of which differed from those cited previously [1] for modification 1: a = 5.40, b = 6.40, c = 11.86 A, $\beta = 91° 23'$, Z = 2; space group $C_{2h}^5 = P2_1/c$. The position of the molecule in the crystal and the atomic coordinates were determined chiefly from Patterson projections along the three crystallographic axes, since the author was unable to obtain satisfactory resolution of the atoms from projections of the electron density. The author interpreted his results on the basis of an assumption of a statistical distribution of noncentrosymmetric molecules or of the presence of pseudosymmetry connected with the very small number of reflections observed.

TABLE 1

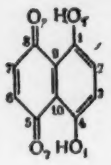
Results of X-ray Measurements of the Three Crystal Modifications of Naphthazarine

Modification	Crystal color and form	Unit cell dimensions				Z	Space group
		a	b	c	β		
1	Dark green needles	3.76	7.72	15.2	109°36	2	$C_{2h}^5 = P2_1/c$
2	Dark red prisms	5.41	6.40	12.86	92°24	2	$C_{2h}^5 = P2_1/c$
3	Light red plates	7.92	7.26	13.8	96°	4	$C_{2h}^5 = P2_1/n$

By crystallization of naphthazarine from solution in benzene, in addition to the two well-known modifications mentioned above, we obtained a third modification (3), the crystals of which were elongated prismatic plates of a light red color.

In Table 1 are presented x-ray data obtained by us for all three modifications of naphthazarine.

It should be mentioned that under conditions such that all three modifications precipitated from solution, well-defined crystals of modification 3 were most frequently encountered. When naphthazarine crystals were prepared by sublimation, modifications 1 and 2 were formed.



I

The assignment of the crystals of modification 1 to the space group C_{2h}^5 = $P2_1/c$ and the presence of two molecules in the unit cell confirm the earlier assumption by the authors cited above [1] of the presence of a center of symmetry in the molecule of a crystal of modification 1.

The inclusion of an internal hydrogen bond O....H−O in the conjugated system of double bonds must cause an essential change in the π-electron interaction throughout the entire molecule, which, in turn, must lead to a redistribution of the electron density in the molecule. In connection with this, it was of interest to carry out a complete x-ray structural analysis of the crystals of this modification.

The synthesis and crystallization of naphthazarine were carried out by Z. P. Glushkova.

In the Patterson projection P (Oyz), the maxima could not be identified with specific interatomic distances in the molecule; however, their distribution along parallel lines forming an angle of ~55° with the axis could be interpreted as the direction characterizing the greatest number of carbon atoms, i.e., the direction coinciding with the extent of C−C and C−O in the molecule. On the basis of this assumption, values of the structure amplitude F (Okl) were calculated for a model of a planar molecule; bond lengths were assumed on the basis of distances agreeing with the structure of Formula I.

After construction of five approximations of electron density projections ρ (Oyz) (Fig. 1), recalculation of the structural amplitudes by means of atomic coordinates obtained from the projections did not lead to a change in the signs nor to an improvement in the value of $R = \Sigma(|F_{exp}| - |F_{calc}|)/\Sigma|F_{exp}|$, which was equal to 0.18 at this stage. The yz coordinates of the atoms relative to an origin located at the center of symmetry of the unit cell are presented in Table 2. The period of the unit cell along the a axis (3.760 A) in the crystal, which is approximately equal to the thickness of the molecule, did not permit a very great diffraction by the molecules of the (100) plane of the crystal.

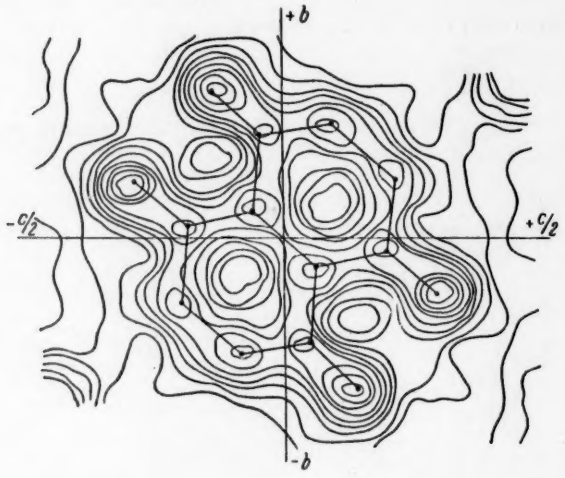


Fig. 1. Projection of the electron density on the yz plane.

On the basis of the atomic coordinates (Table 2) obtained from the electron density projections ρ (Okl), bond lengths between the atoms in molecule (II) were calculated.

TABLE 2

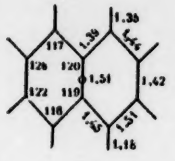
Atomic Coordinates (yz) Calculated from Electron Density Projections ρ (Oyz)

Atom	y/b	z/c	Atom	y/b	z/c
$C_{(1)}$	0.0195	0.132	C(10)	0.062	0.050
$C_{(2)}$	0.835	0.144	O(1)	0.130	0.198
$C_{(3)}$	0.713	0.072	O(2)	0.341	0.087
$C_{(4)}$	0.245	0.029			

The calculations were carried out on the assumption that the molecule is disposed parallel to the yz plane. The angle formed by the line of the C_9-C_{10} bond in the molecule and the y axis of the unit cell is 50°. The closest distance between carbon and oxygen atoms in different molecules is 3.10 A.

As seen from the x-ray structural analysis data presented, the presence of a center of symmetry in the molecule of naphthazarine modification 1 is confirmed. The structure of the napthalene nucleus in this case is dependent on the nature of the bonds between the carbon and oxygen atoms, of which the first is a double bond (1.1817 A) and the second is an ordinary bond (1.35 A).

As seen from the above, during crystallization from solution, all three modifications simultaneously precipitate: two centrosymmetric (A) and one noncentrosymmetric (B) modifications. Recrystallization of any of these modifications again leads to the formation of the three indicated modifications (in fact, frequently with a predominance of some one of these types). Therefore, it may be proposed that a conversion of the isomer with structure A to the isomer with structure B (and vice versa) takes place, as shown in III; this was previously proposed in a paper by D. N. Shigorin and H. S. Dokunikhin [4].

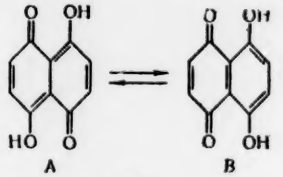


II

These authors, investigating the spectra of naphthazarine vapors, observed the presence of two bands corresponding to valence vibrations of the OH group, which confirms the existence of an equilibrium between the indicated isomers.

It should be noted that our orientation of the molecule in the yz plane is quite consistent with the orientation of the molecule given in the paper by Billy [3] for crystals of centrosymmetric modification 2.

In order to obtain the third coordinate x and to increase the accuracy of the results, it would be necessary to carry out a three-dimensional analysis.



III

We take pleasure in expressing our appreciation to N. S. Dokunikhin and D. N. Shigorin for valuable advice during the course of the work and consideration of the results.

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